

AD-A224 551

REPORT DOCUMENTATION PAGE			Form Approved GSA No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 30 June 1990	3. REPORT TYPE AND DATES COVERED Final 1 Jul 86 - 30 Apr 90		
4. TITLE AND SUBTITLE Electrochemistry of Metal Surfaces		5. FUNDING NUMBERS 61102F 2303/AJ		
6. AUTHOR(S) Arthur T. Hubbard		DTIC FILE COPY (2)		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Cincinnati Department of Chemistry Cincinnati, OH 45221-0172		8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR 90 0838		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Building 410 Bolling AFB, DC 20332-6448		10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFOSR-86-0200		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) See Back <div style="text-align: center;"> DTIC ELECTE JUL 26 1990 S <i>cc</i> D </div>				
14. SUBJECT TERMS		15. NUMBER OF PAGES 53		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

13 The essence of this AFOSR project is investigation of the structure, composition, mode of attachment and reactivity of the surface molecular species which form when metals come into contact with fluids. A series of findings, advances in investigative technology and 91 scientific articles have occurred thus far during this project. These include: i) determination of the orientations and modes of attachment of organic molecules attached to electrode surfaces; ii) demonstration that each orientation of an adsorbed molecule manifests different chemical and electrochemical reactivity; iii) discovery that electrodeposition of metals at single-crystal surfaces produces highly-ordered layers; iv) discovery that contact between metal surfaces and ionic solutions forms chemically unique, ordered layers; v) adaptation of electron energy-loss spectroscopy (EELS) for measurement of vibrational spectra of molecules adsorbed at metal surfaces from solutions; vi) systematic study of 150 adsorbed phenols, acids, amines, pyridines, mercaptans, alcohols, alkenes and aromatics as to structure (LEED), composition (Auger), molecular construction/mode of surface attachment (EELS), chemical reactivity (all methods), and electrochemical reactivity (cyclic voltammetry, CV); vii) demonstration of the stability of these adsorbed layers toward vacuum and electron beams used in surface spectroscopy by performing CV before and after the electron spectra were obtained; and, viii) studies of surface structure by means of Auger electrons. These results have practical usefulness as well as fundamental significance: any substance present in any practical amount on virtually any solid metal surface can now be identified, quantitated and characterized; chemisorbed intermediates can be characterized and their electrochemical reactivity can be explored; molecular species formed at metal surfaces as a result of lubrication, corrosion, immersion, electrolysis, adhesive action, combustion and other high pressure processes can now be characterized as to composition, molecular structure, mode of surface attachment, and other physical and chemical properties; and studies begun with Pt surfaces have now been extended to various non-noble metals.

FINAL TECHNICAL REPORT
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
BOLLING AIR FORCE BASE, D.C. 20332-5448

1. Date Submitted June 30, 1990
2. Title: Electrochemistry of Metal Surfaces
3. Previous Grant Number: AFOSR 86-0200
4. Report Period: May, 1986 through April, 1990
5. Amount Awarded: \$415,232
6. Institution Name University of Cincinnati
 Department of Chemistry
 Cincinnati, OH 45221-0172

Congressional Districts 1 and 2.

Employer ID Number: 31-6000989W

7. Principal Investigator: Arthur T. Hubbard
 Professor of Chemistry
 Telephone (513) 559-1090

Approved for public release;
distribution unlimited.

TABLE OF CONTENTS

Abstract	3
I. Report of Research	4
A. Some Motivations for Research in Surface Electrochemistry	4
B. Adsorption and Reactivity of Pyridine Derivatives at Pt(III)	5
C. Conformation and Reactivity of Amino Acids at Pt(III)	13
D. Adsorption and Reactivity of Phenols at Pt(III)	14
E. Sulfide at Pt(III) and Pt(100)	16
F. Comparison of Annealed and Cycled Pt Surfaces	16
G. Adsorption and Reactivity of Unsaturated Alcohols at Pt(III)	17
H. Thiophene Derivatives as Monomers and Polymers at Pt(III)	18
I. 2,2'-Bipyridyl Derivatives as Pt(III)	19
J. Halide Films at Ag(III) Electrodes	20
K. Electrodeposition of Bi, Tl, Pb and Cu at Ag(111) Electrodes	21
L. Alkenoic Acids at Pt(111)	21
M. Multinitrogen Heteroaromatics at Pt(111)	22
N. Alkenols at Pt(111)	23
O. Alkenes at Pt(111)	25
P. Comparison of EELS and IR Spectra	28
Q. Imaging Metal Surface Atomic Structure	30
R. Some Implications of These Results	31
II. Publications	34
III. References to Other Work	51
IV. Scientific Personnel	52
V. Current Support	53

Accession For	
NTIS	<input checked="" type="checkbox"/>
CRA&I	<input type="checkbox"/>
DTIC	<input type="checkbox"/>
TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	



ABSTRACT

The essence of this AFOSR project is investigation of the structure, composition, mode of attachment and reactivity of the surface molecular species which form when metals come into contact with fluids. A series of findings, advances in investigative technology and 91 scientific articles have occurred thus far during this project. These include: i) determination of the orientations and modes of attachment of organic molecules attached to electrode surfaces; ii) demonstration that each orientation of an adsorbed molecule manifests different chemical and electrochemical reactivity; iii) discovery that electrodeposition of metals at single-crystal surfaces produces highly-ordered layers; iv) discovery that contact between metal surfaces and ionic solutions forms chemically unique, ordered layers; v) adaptation of electron energy-loss spectroscopy (EELS) for measurement of vibrational spectra of molecules adsorbed at metal surfaces from solutions; vi) systematic study of 150 adsorbed phenols, acids, amines, pyridines, mercaptans, alcohols, alkenes and aromatics as to structure (LEED), composition (Auger), molecular construction/mode of surface attachment (EELS), chemical reactivity (all methods), and electrochemical reactivity (cyclic voltammetry, CV); vii) demonstration of the stability of these adsorbed layers toward vacuum and electron beams used in surface spectroscopy by performing CV before and after the electron spectra were obtained; and, viii) studies of surface structure by means of Auger electrons. These results have practical usefulness as well as fundamental significance: any substance present in any practical amount on virtually any solid metal surface can now be identified, quantitated and characterized; chemisorbed intermediates can be characterized and their electrochemical reactivity can be explored; molecular species formed at metal surfaces as a result of lubrication, coating, immersion, electrolysis, adhesive action, combustion and other high pressure processes can now be characterized as to composition, molecular structure, mode of surface attachment, and other physical and chemical properties; and studies begun with Pt surfaces have now been extended to various non-noble metals.

I. REPORT OF RESEARCH

A. Some Motivations for Research in Surface Electrochemistry.

Before proceeding to a discussion of recent studies of pyridine derivatives, let us take a few moments to reflect on the underlying reasons for making studies of this type. There is a need to detect, identify and quantitate the species which form at metal surfaces under conditions typical of practical situations such as bonding of materials, protection of metal surfaces, lubrication of metals, storage of electrical energy, cleaning of materials, fabrication of electronic devices and sensors, and others. Thus far, we have adapted LEED, Auger spectroscopy, EELS, surface IR spectroscopy and voltammetry/coulometry for this purpose, and we will continue to invest part of our time in improvements of investigative methodology. With these methods we can detect, quantitate and identify virtually any surface species in any practical amount.

Identification of surface species (atoms, ions, molecules and oligomers) will be an important aspect of any future discovery, development and testing of new surface-related processes and devices by designed approaches rather than trial and error. Investigation of the mode of bonding of chemical substances and materials to surfaces provides valuable clues by which to understand the behavior of metallic and other solid surfaces in contact with fluids. Substrate surface characterization (structure, cleanliness, electronic properties) is becoming increasingly important with the continuing discovery of examples of substantial influences of roughness, trace elements, and other surface characteristics. Knowledge of the relative affinities of various classes of chemical substances for various categories of material surfaces is essential to design of surface-related processes and devices. Exploration of chemical families of well-characterized adsorbed species by various forms of surface-sensitive spectroscopy both in surveys and in detailed studies is vital to future explorations of surface processes and phenomena. Observations of the chemical reactivity and electrochemical redox of well-characterized adsorbed layers, and of the influence of such species on the reactions of unadsorbed reactants are reliable benchmarks of the surface sciences, including electrochemistry. Results from various laboratories around the world are adding emphasis to the realization that surface structure is an important factor in electrode reactions of organic molecules, and to the need for electrode surface characterization.

B. Adsorption and Reactivity of Pyridine and Derivatives at Pt(111).

Pyridine and its derivatives belong to a class of compounds which adsorb strongly at Pt electrodes in a vertical orientation with the plane of the ring approximately perpendicular to the surface (47). Evidence for vertical orientation of pyridine adsorbed from vacuum at low temperature and warmed to room temperature has also been reported (162–165). Accordingly, we undertook to study pyridine and some of its typical derivatives as an opportunity to learn about vertically-oriented adsorption and to compare it with the equally important horizontally-oriented adsorption of aromatic compounds (117).

Our latest studies of pyridine and its derivatives at Pt(111) electrode surfaces by means of LEED, Auger, EELS and voltammetry (125) have confirmed the vertical orientation but have produced some remarkable surprises, as well:

(i) 3-pyridine carboxylic acid (nicotinic acid, NA) binds to Pt surfaces through both the nitrogen atom and an oxygen atom of the carboxylate group when adsorption is carried out at relatively positive potentials. When adsorbed at relatively negative potentials NA binds exclusively through the N atom and has a highly active carboxylic acid pendant. These principles were deduced initially from EELS spectra which showed a prominent O–H stretch at 3566 cm^{-1} , Figure 1–A, which disappeared at positive potentials, Figure 1–B. This transition between coordinated and pendant carboxylate occurs smoothly with potential, and is not due to deposition of NA, as illustrated by the EELS and Auger data shown in Figure 2.

(ii) Evidence of the potential-dependence and pendant acidity of NA is seen in the retention of K^+ by the NA layer in alkaline solutions, Figure 3. K^+ ions are retained only at relatively negative potentials, in agreement with the implications of the EELS data. The pK_A of NA is less than 4. We have not yet devised an accurate method of measuring pK_A for such a favorable acid dissociation. This very active pendant invites utilization for a wide variety of fundamental studies and practical chemical modifications of surface behavior.

(iii) Pyridine adsorbs at virtually constant packing density ("coverage") at all dosages from 0.1 mM all the way to neat liquid pyridine, and displays a clear but complex LEED pattern shown in Figure 4. This LEED pattern corresponds to a Pt(111) $(3.324 \times 4.738, 77.1^\circ)\text{R}34^\circ\text{--PYR}$ unit mesh. In matrix notation this is:

$$\begin{bmatrix} a_1 & a_2 \\ b_1 & b_2 \end{bmatrix} = \begin{bmatrix} 1.684 & 2.145 \\ -4.255 & 5.106 \end{bmatrix}$$

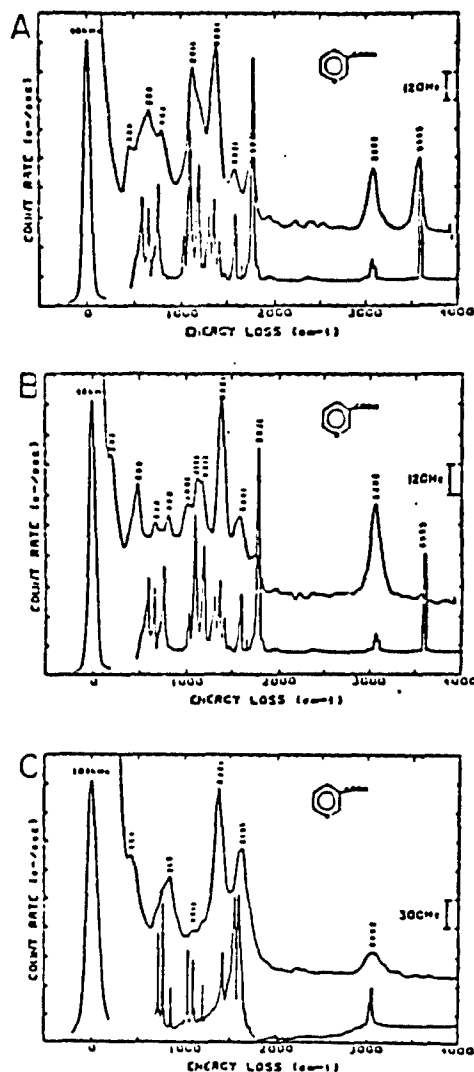


Figure 1 Vibrational spectra of NA.

- A. EELS spectrum of NA adsorbed at Pt(111), $-0.2V$, pH 3.
Lower curve in A and B is mid-IR spectrum of NA vapor (19).
- B. EELS spectrum of NA at Pt(111), $+0.6V$, pH 3.
- C. EELS spectrum of NA at Pt(111), $-0.3V$, rinsed at pH 10.
Lower curve is mid-IR spectrum of solid KNA.

Experimental conditions: adsorption from $1mM$ NA in $10mM$ KF, pH 3 (A and B) or pH 7 (C), followed by rinsing with $1M$ HF (A and B, pH 3) or $0.1mM$ KOH (pH 10, C); EELS incidence and detection angle 62° from surface normal; beam energy, $4eV$; beam current about $120pA$; EELS resolution, $10meV$ ($80cm^{-1}$) F.W.H.M.; IR resolution, $4cm^{-1}$.

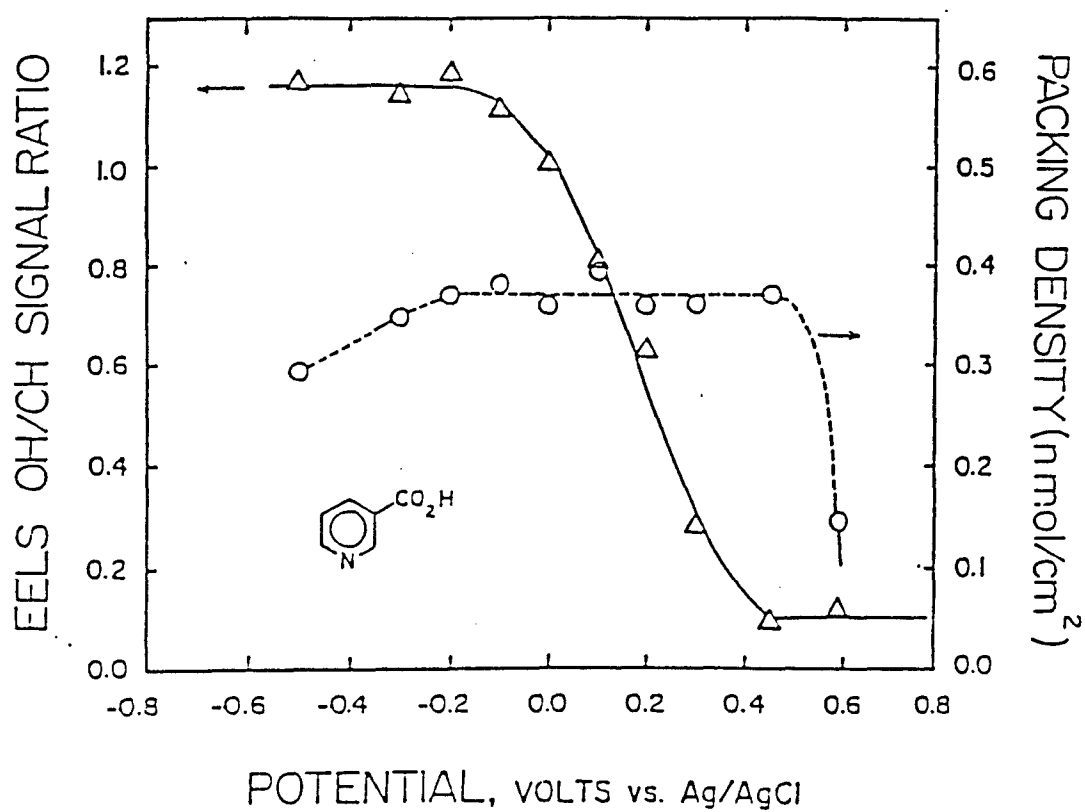


Figure 2. Ratio of EELS O-H (3566cm^{-1}) to C-H (3068cm^{-1}) peak height (Δ); Packing density of NA (\circ).

Experimental conditions: adsorption from 1mM NA in 10mM KF at pH 7, followed by rinsing in 2mM HF (pH 3); electron beam at normal incidence, 100nA, 2000eV.

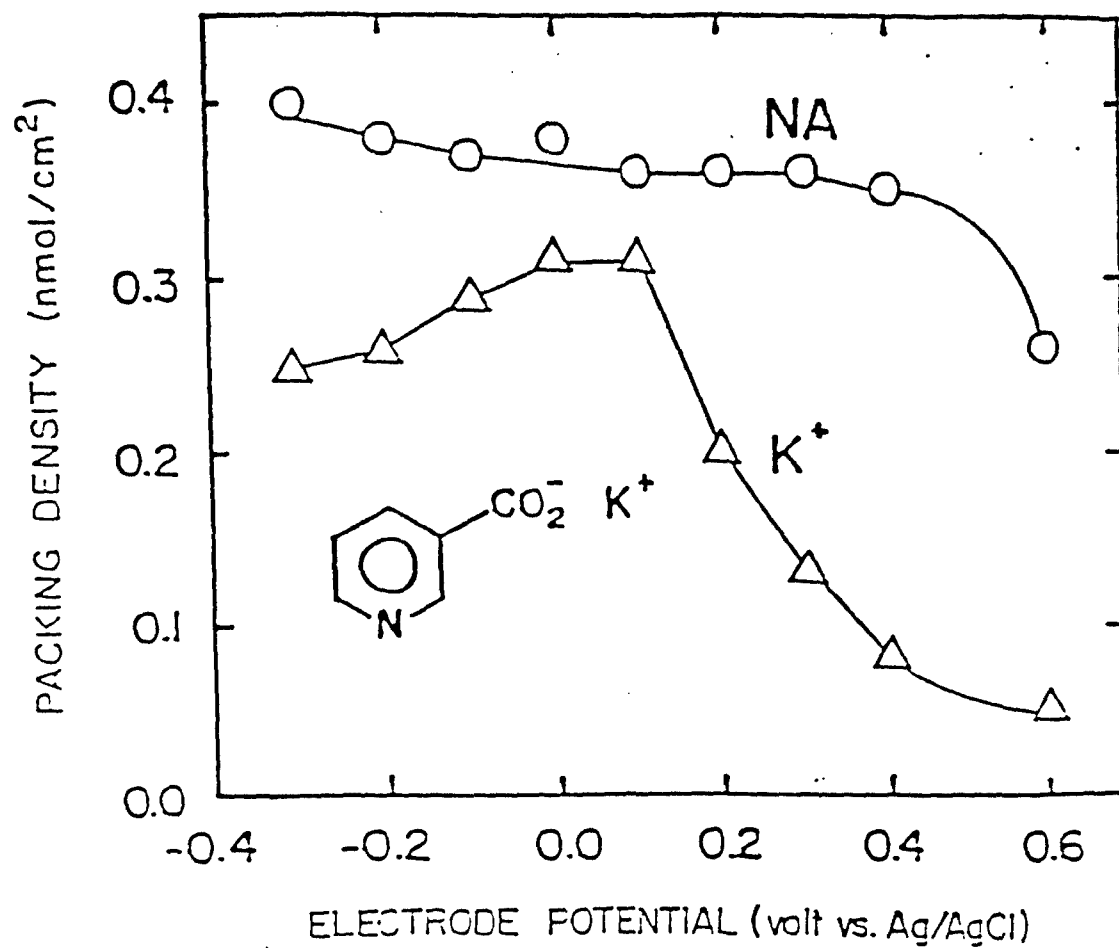


Figure 3. Packing density of K⁺ ions (Δ); packing density of NA (o).
 Experimental conditions: adsorption from 1mM NA in 10mM KF (pH 3),
 followed by 3 rinses in 0.1mM KOH (pH 10). EELS conditions as in Figure 1
 Auger conditions as in Figure 2.

Pt(111)(3.324 x 4.738, 77.1°)R34.0°-PYR

1.684	2.145
-4.255	5.106

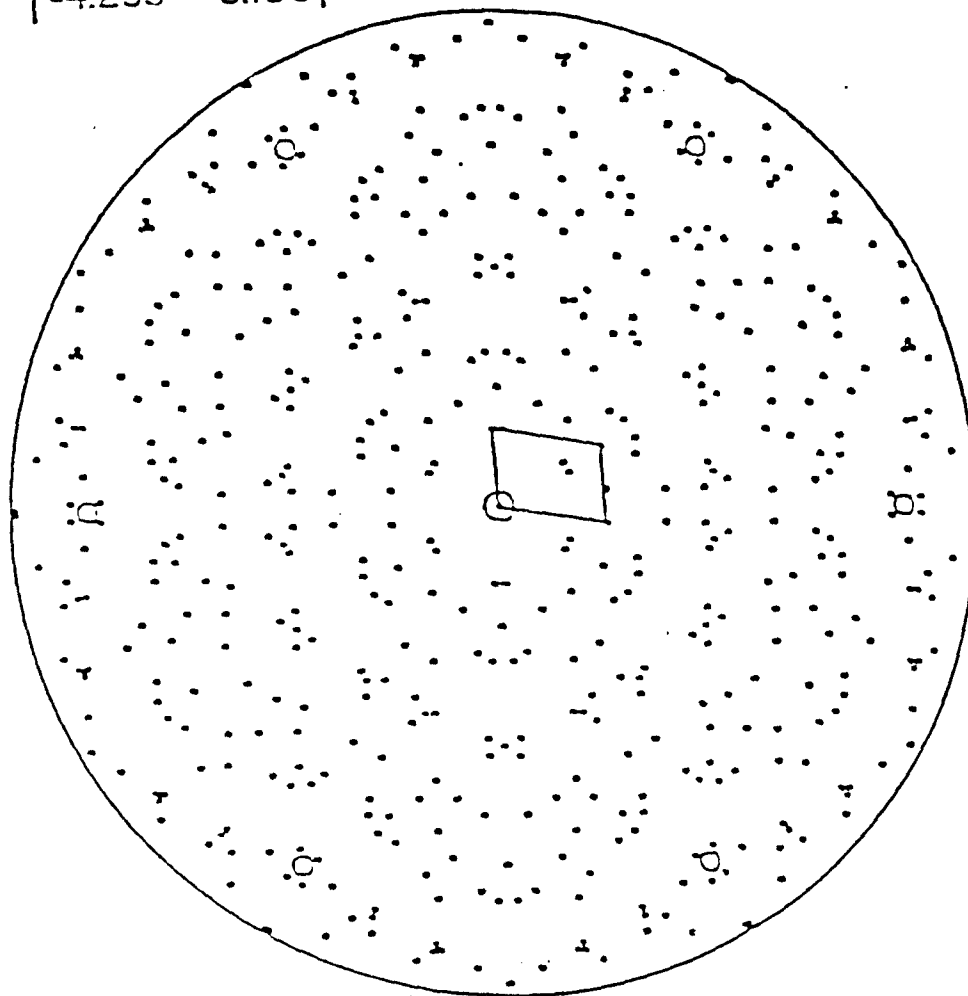


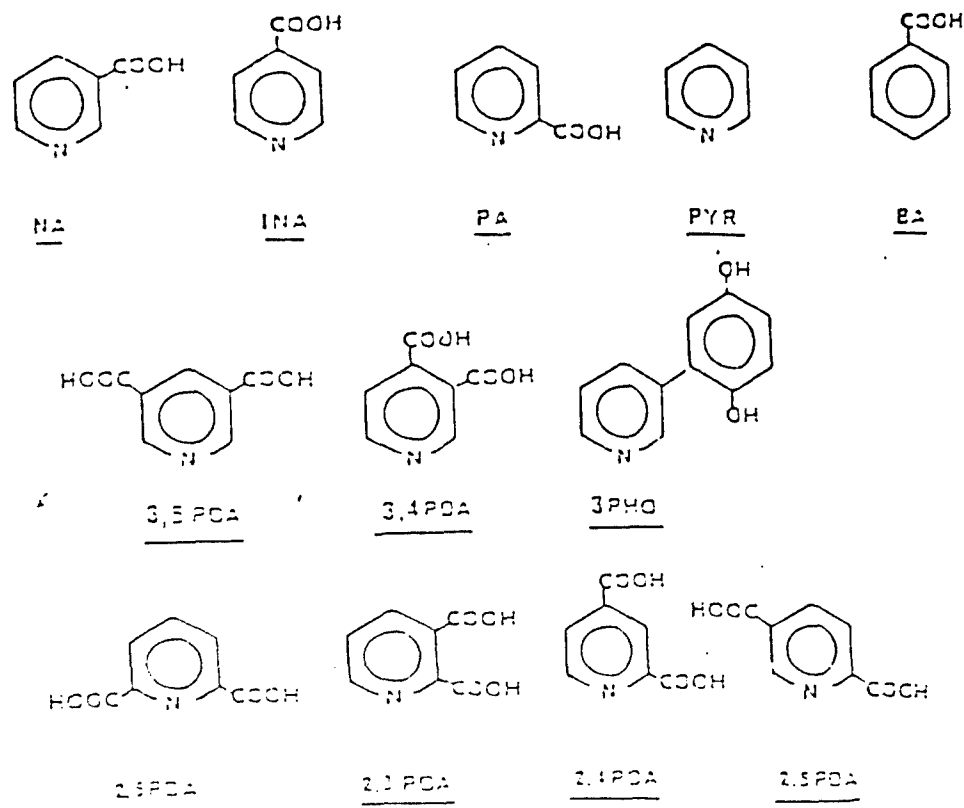
Figure 4. Diagram of the LEED pattern of PYR adsorbed at Pt(111), 51eV. Experimental conditions: adsorption from 1mM PYR in 10mM KF (pH 7) at -0.3V, followed by rinsing with 0.1mM KF (pH 7).

This is an incommensurate structure in which the pyridine molecules do not have integral periodicity with respect to the Pt surface atoms. The nearest commensurate structure, $(2\frac{1}{3} \times \frac{1}{2}, 79^\circ)R30^\circ$, and all other commensurate structures correspond to expected LEED patterns dramatically different from the observed pattern. Likewise, changes in the mesh vectors by more than about 0.1% from those stated above predict noticeably different patterns. Pyridine (and quite possibly its derivatives) favors an incommensurate (but ordered and oriented) structure.

(iv) Remarkable inertness of Pt-pyridine and Pt-NA monolayers is illustrated by the cyclic voltammograms in Figure 5. A horizontally-oriented adsorbate, benzoic acid, is relatively reactive by comparison, Figure 5-C.

(v) Packing densities of pyridine and derivatives are consistently intermediate between that expected for horizontal and perpendicular-vertical orientations, as illustrated by Figure 6. The angle, Θ , between the ring and the Pt surface is 70 to 75° for all of the pyridine derivatives studied. This tilted structure is consistent with the potential-dependent coordination behavior of NA, and as we shall see is also consistent with the behavior of the other compounds studied.

(vi) Studies similar to items (i - v) above were also carried out for all of the compounds shown below:



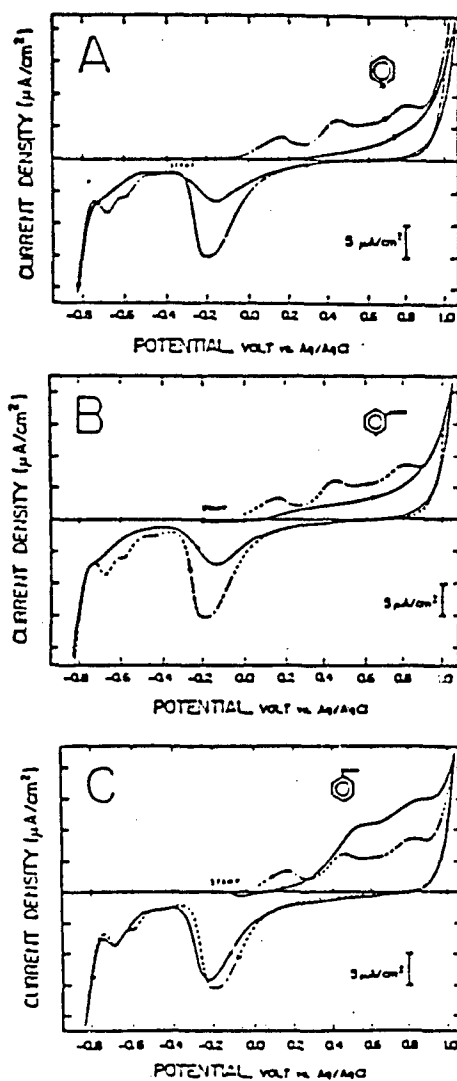


Figure 5. Cyclic voltammetry at Pt(111).

A. PYR

B. NA

C. BA

(—) Solid curves: adsorbed layer; (---) dashed curve: clean Pt(111).

Experimental conditions: adsorption from PYR (0.1mM, -0.1V), NA (1mM, -0.2V), or BA (1mM, -0.1V) in 10mM KF (pH 7); rinse and scan in 10mM KF (pH 7); 5mV/S.

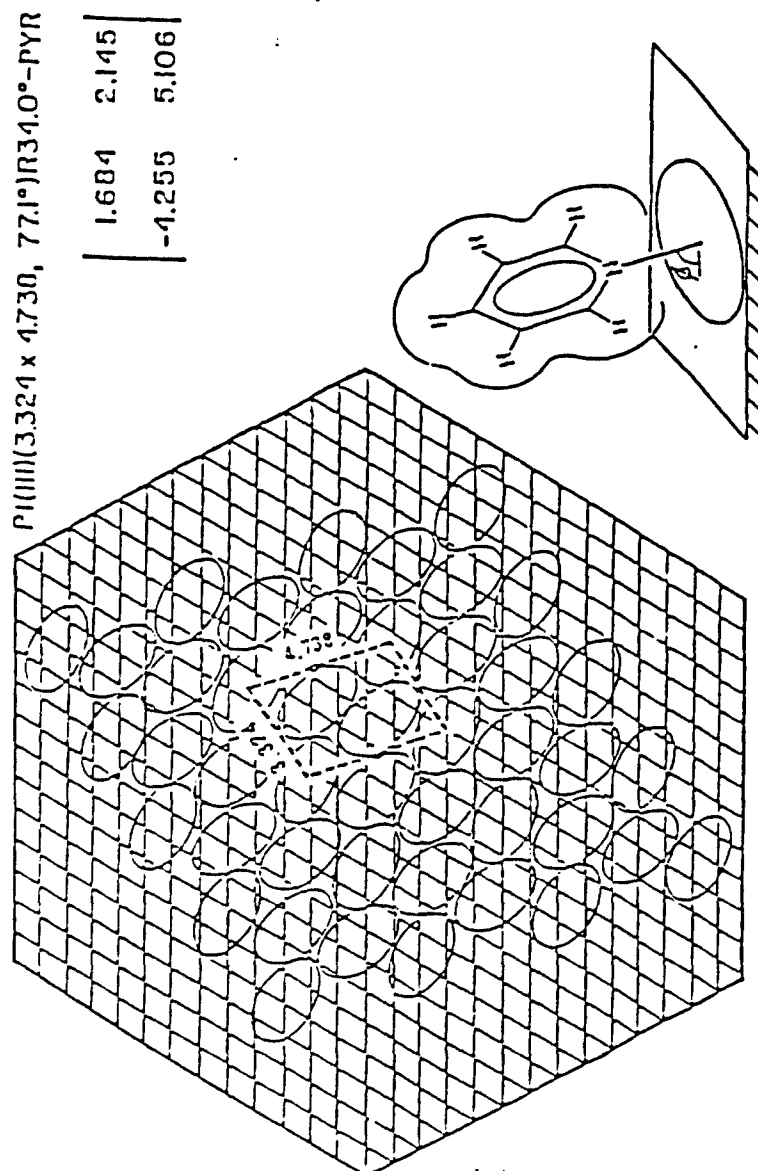


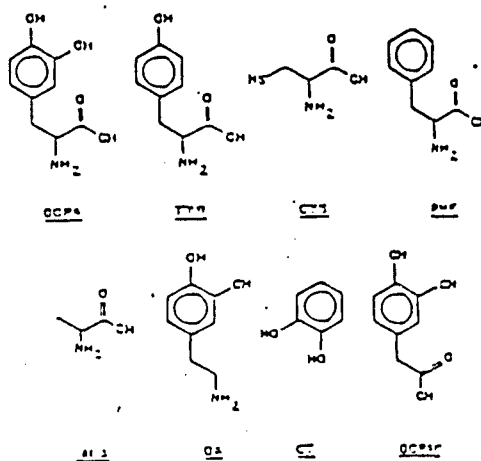
Figure 6. Model of the $\text{Pt(III)}(3.324 \times 4.730, 77.1^\circ)\text{R}34.0^\circ\text{-PYR}$. The PYR packing density in this model is 0.421 nmol/cm^2 .
 Experimental conditions: adsorption from 1 mM PYR in 10 mM KF ($\text{pH } 7$) at -0.3 V , followed by rinsing with 0.1 mM KF ($\text{pH } 7$).

In a few words, the results are: carboxylate of INA is pendant at all potentials, as expected from the para structure of INA; on the other hand, the PA carboxylate group always interacts with the Pt surface, as expected from its proximity to the N and Pt. Similar trends are exhibited by the various pyridine dicarboxylic acids.

(vii) Cyclic voltammetry of the (3-pyridyl)hydroquinone adsorbed layer before and after one hour in vacuum yielded virtually identical results. A small decrease in background current was the only effect of evacuation. Experiments were also performed in which LEED, Auger and EELS were performed prior to voltammetry. Again, the voltammetric results were the same. The pyridine anchor and the hydroquinone pendant are sufficiently stable in vacuum and electron beams to allow their study by the methods we use. Please refer to Reference 125 for details.

C. Molecular Conformations and Reactivity of Amino Acids at Pt(111).

Combining the AFOSR instrumentation with operating support from the National Institutes of Health has allowed us to follow up the pyridine studies with further substantiation from studies of aromatic amino acids and related fragments (121):



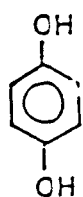
The essence of our findings is as follows: Two planes were studied to give us an indication of the influence of surface plane on adsorption and reactivity, namely, Pt(111) and Pt(100). Packing densities measured by two Auger spectroscopic methods indicate adsorption of DOPA, TYR, DA, CT and DOPAC with the aromatic ring parallel to the Pt surface. The side chains tend to be pendant at Pt(100) and coordinated at Pt(111), based upon packing densities. As a result, oxidation of the adsorbed layer is more extensive (larger n_{ox}) at

Pt(111) than at Pt(100). In contrast, CYS is adsorbed through the S atom, while ALA and PHE are attached through their amino acid moieties. Evacuation does not influence the voltammetric behavior of the adsorbed layers of these compounds. Vibrational (EELS) spectra of these adsorbed species reveal that the hydroxyl hydrogens of DOPA, TYR, DA, CT and DOPAC as well as the carboxylhydrogens at PHE and DOPAC, all horizontally oriented adsorbates, are partially or completely removed as a result of the adsorption process. CT forms an ordered layer at Pt(111), but the others do not have long range order as judged by LEED. Competition among the acid, amine, amino acid and aromatic moieties of these compounds for coordination to the surface is thus a function of the structure of the surfaces, resulting in a strong dependence of bonding and reactivity of surface species on surface structure. Details and further analysis of the results are given in References 121 and 128.

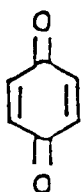
D. Adsorption and Reactivity of Phenols at Pt(111):

Studies were made of a group of phenols with respect to their adsorption at Pt(111), packing density and stoichiometry as judged by Auger spectroscopy, vibrational frequencies as judged by EELS, and electrochemical reactivity by use of voltammetry and coulometry (117, 119). Phenols were chosen for study because hydroquinone and catechol are electroactive and water soluble, allowing their study by electrochemical methods as well as the more general electron and photon spectroscopic techniques. Our goal in studying the phenols is of course to understand the surface electrochemistry and catalytic chemistry of aromatic compounds. These phenols are yielded results which have moved us substantially in the direction of our goal, and have served as a connecting link between electrochemical studies (described in about 45 AFOSR-supported publications) and the newer electron spectroscopic investigations. Details are given in References 117 and 119. Only a brief synopsis will be attempted here.

The compounds studied are:



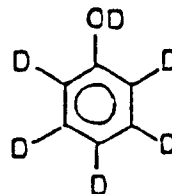
HQ



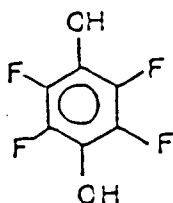
BQ



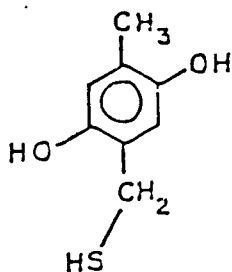
PL



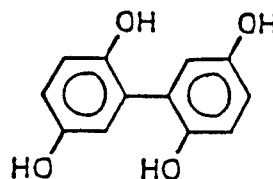
PDPL



TFHQ



DMEM



THBP

Packing densities measured by two independent Auger methods indicated adsorption of HQ, BQ, PL, DPDL and TFHQ with the ring parallel to the Pt(111) surface, while DMBM was attached through the sulfur atom with the ring pendant from the surface. EELS spectra of these adsorbed compounds are virtually the envelope of the IR spectrum, except that the OH hydrogens are partially or completely removed as a result of adsorption. Horizontal orientations of all but DMBM are much more stable at Pt(111) than at polycrystalline surfaces (47). Studies of deuterated compounds such as PDPL confirmed the EELS assignments based upon the IR spectroscopy literature, and demonstrated the purity of the adsorbed layer. HQ, BQ, PL and PDPL displayed substantial long-range ordering when adsorbed from dilute aqueous solutions. DMBM displayed reversible quinone—hydroquinone electroactivity in the adsorbed state. THBP formed a mixed layer,

the vertical component of which was electroactive. Electro-oxidation of adsorbed HQ, BQ, PL, and PDPL preceded irreversibly but completely to CO_2 . No significant changes in electroactive behavior of these adsorbed compounds occurred as a result of evacuation or electron spectroscopic characterization under the conditions of these experiments: electron spectroscopy is applicable to the study of typical aromatic compounds adsorbed at electrode surfaces.

E. Sulfide at Pt(111) and Pt(100):

AFOSR funded instrumentation was employed for study of the processes which take place when metals are treated with aqueous sulfide solutions (127). Voltammetry revealed that oxidative desorption of adsorbed S occurs at relatively positive potentials (primarily as SO_4^{2-} ions) but reductive desorption did not occur to a detectable extent. Absence of K^+ ions (based upon Auger spectroscopy) followed adsorption from K_2S solutions is evidence that the layer is composed of a neutral Pt S coordination compound. Adsorbed sulfur layers are highly ordered under all conditions of adsorption where the S layer is stable. LEED patterns are Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-S and Pt(100)($\sqrt{2} \times \sqrt{2}$)R45°-S. In particular, sulfide is one of the few adsorbates studied thus far which forms a primitive, highly ordered structure at room temperature on the otherwise complicated Pt(100) surface. EELS spectra of the sulfur layer have identified the Pt-S vibrational modes of these interesting adsorbed layers.

F. Comparison of Annealed and Electrochemically-Cycled Pt Surfaces.

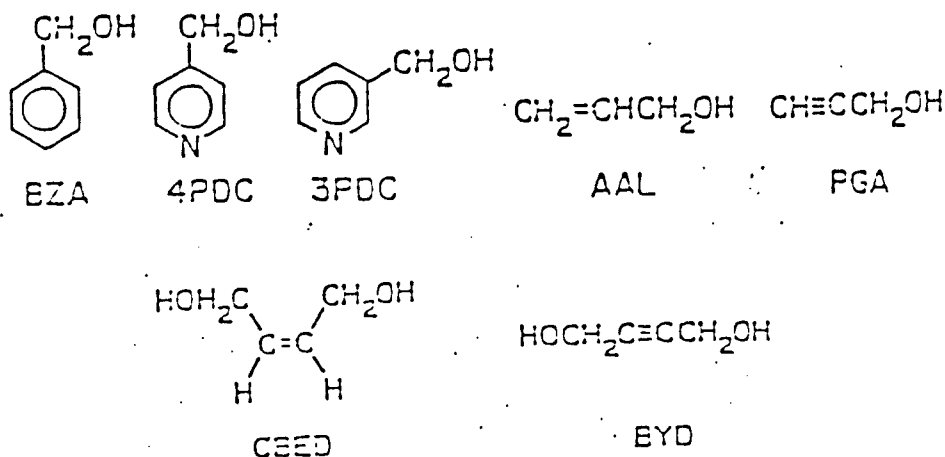
An intriguing series of experiments has been performed in which packing density, electrochemical reactivity and surface vibrational spectra are compared for various typical adsorbates at annealed Pt(111) and electrochemically-cycled Pt(111) surfaces (126,137). By "cycled" is meant the repeated oxidation (+1.4 V vs. Ag/AgCl) and reduction (-0.2 V) process by which electrochemists commonly clean their electrode surfaces.

The purpose of these experiments is, of course, to reveal the effects which the cycling process might have upon the nature of adsorbed species and electrocatalytic reactivity as judged by EELS, Auger spectroscopy, and voltammetry. Future work will add polycrystalline surfaces to the single-crystal surfaces already studied. Compounds

studied to date are: HQ, THBP, DMBM, 3PHQ, NA and 3-thiophene carboxylic acid (3TCA). Very striking differences are observed between annealed and cycled surfaces in all respects: electrochemical reactivity, vibrational spectroscopy and quantitative aspects (126,137). Elastic, specular reflection of slow electrons from the Pt surface is diminished 30-fold by cycling, evidence of surface roughness. Vibrational intensities and frequencies are profoundly altered. For instance, aromatic C-H stretching increases upon cycling, while O-H stretching in the pendant groups decreases. Spectral changes are greatest for HQ and THBP bound to the surface primarily in horizontal orientations, in contrast to the vertically oriented adsorbates DMBM, 3PHQ, NA and 3TCA. Evidently, cycling influences the bonding of the HQ aromatic ring to the Pt surface, leading to more pronounced spectral changes than for the vertical adsorbates which undergo less contact between the aromatic ring and the surface. Packing density as measured by Auger spectroscopy changes as a result of cycling. This is further indication that cycling causes profound changes in surface and adsorbed layer geometric structure and electronic properties.

G. Adsorption and Reactivity of Unsaturated Alcohols at Pt(111).

Unsaturated alcohols provide an opportunity to view the interplay between two competing adsorbates (OH and C=C) in the same layer, as well as between the electrochemical reactants in the same molecule (132). Also, this marks one of our first inroads into the study of neat organic liquids at well-defined surfaces. Compounds included in this initial study were:

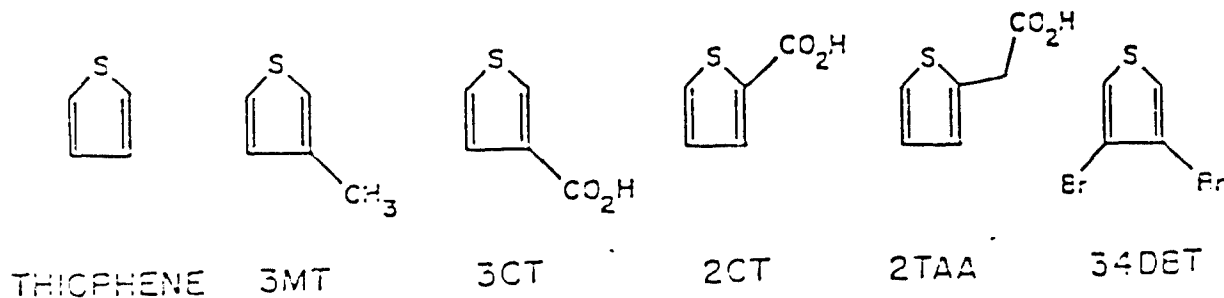


Chemisorption of the unsaturated center of each compound proves to be the principal mode of surface attachment (phenyl, pyridyl, alkenyl or alkynyl moiety). Electrochemical oxidation of adsorbed BZA, AAL, PGA, CBED and BYD in aqueous fluoride electrolyte proceeds efficiently to CO_2 , while adsorbed 4PDC and 3PDC are relatively inert. Evidently, the pyridine ring keeps the alcohol moiety out of contact with the pt surface. Oxidation of BZA, AAL, PGA, CBED and BYD in each case begins with the alcohol moiety, followed by oxidation at more positive electrode potentials of the unsaturated point-of-attachment to the surface. The adsorbed layer of each of these alcohols is stable in vacuum, such that surface spectroscopic methods in vacuum are directly applicable to the liquid-solid interfacial chemistry and electrochemistry of these compounds. 4PDC and 3PDC are adsorbed in a tilted vertical orientation, analogously to pyridine. The triple bonds of PGA and BYD are evidently converted quantitatively to double-bonds as a result of the adsorption process. However, the aromatic and alkene and alkene groups of adsorbed BZA, 4PDC, 3PDC, AAL and CBED remain essentially intact, with only small shifts in their vibrational frequencies (EELS).

H. Thiophene and Derivatives as Monomers and Polymers at Pt(111).

Thiophene and its derivatives polymerize relatively easily at an electrode surface under mildly oxidizing conditions in an aprotic solvent such as acetonitrile (166-171). Acetonitrile adsorbs strongly at transition metal surfaces (42,45), and this would be expected to compete with the polymer for attachment to the surface (105). Likewise, the thiophene monomers could attach to the surface prior to polymerization (172,173). In order to better understand the nature of the electrogenerated polymers and the role of solvent, monomer and electrolyte in polymer attachment to a solid surface, we have undertaken studies of thiophene monomers and polymers at Pt(111) surfaces using LEED, Auger, EELS and electrochemistry (129). Surface infrared spectroscopy will be performed in the near future on these layers.

Compounds studied to date are:

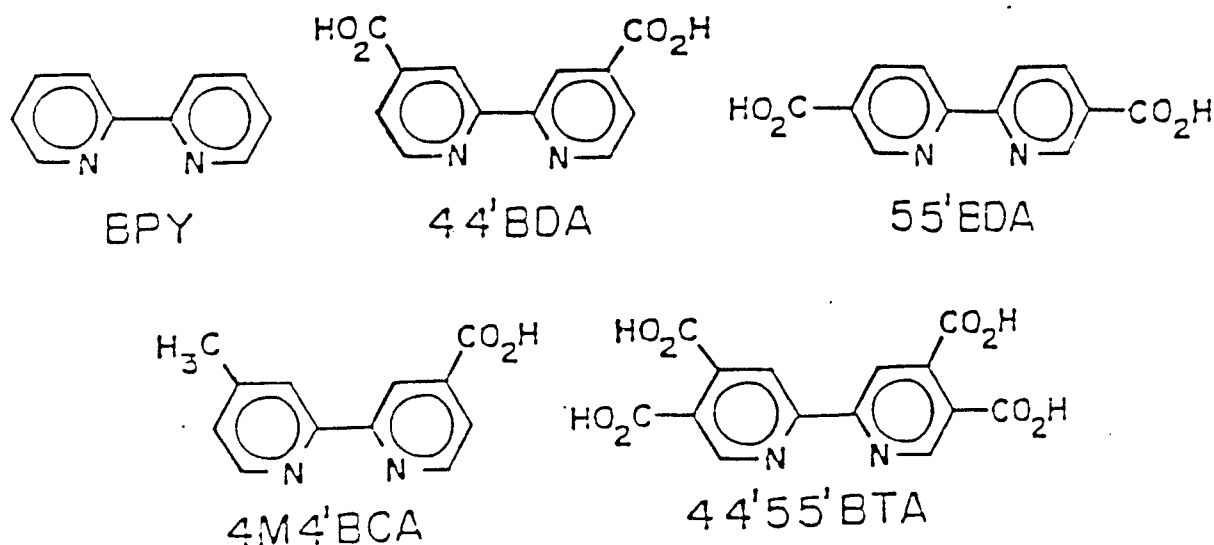


Each of these compounds proves to be strongly adsorbed at Pt(111) from aqueous solutions in a close-packed layer of tilted vertical orientation. However, adsorption from acetonitrile solutions occurs only at much higher concentrations (greater than 0.1 M) than were previously employed for electropolymerization reactions. Adsorbed monomer remains attached under the conditions used for polymerization. Evidently, filming of an electrode surface occurs in spite of the presence of a pre-adsorbed layer of solvent and/or monomer! Pendant carboxylate groups are present in the monomeric layer of 3CT, 2CT or 2TAA. Some coordination of carboxylate groups to Pt occurs at positive electrode potentials, but to a lesser extent than for NA and related pyridine derivatives. Accordingly, thiophene monomers and polymers are also excellent anchors for functional group attachment to surfaces. Unfortunately, some desulfurization occurs during adsorption. 34DBT has the interesting property that its electropolymerized film is relatively free of C-H bonds, as evidenced by EELS spectra of the polymer. Relatively inert and very adherent polymeric films might therefore be possible from monomers of this type. We are at a preliminary stage on this topic, and work is continuing.

I. 2,2'-Bipyridyl and Derivatives at Pt(111).

In collaboration with Professor Michael Elliot (Colorado State University) we are investigating 2,2'-bipyridyl and derivatives at Pt(111) (133).

Compounds studied to date are:



The objective of these studies was to determine whether the placement of the nitrogen atoms in BPY permits binding of both rings to the Pt surface in the usual tilted-vertical orientation. It does. We also experimented with the potential-dependence of the acid O-H stretching bonds in 44'BDA, 55'BDA, 4M4'BCA, and 44'55'BTA. Coordination of the carboxylate groups to Pt is less extensive in the PBY derivatives than in pyridine derivatives and chemisorption of BPY is weaker than pyridine.

J. Halide Films at Ag(111) Electrodes.

Along with future studies of noble metal surfaces our plans include non-noble metals and alloys. Studies of single-crystal stainless steel alloys were reported previously (81,83,85,109). Silver (114,115) and eventually silver alloys are another important avenue for future study.

Studies have been made by means of Auger spectroscopy, LEED, and voltammetry of the surface layers which are formed when an Ag(111) surface is immersed into aqueous halide solution (KF, KCl, KBr and KI) at controlled pH, and electrode potential. The full range of electrode potentials was explored (from water reduction to silver dissolution). Two pH's were studied: 4 and 10. Surface composition was monitored by means of quantitative Auger spectroscopy. Seven elements, F, Cl, Br, I, O, K and Ag entered into these studies. Strong adsorption of Cl, Br and I occurs throughout most of the potential range. F and K adsorption is negligible. Oxygen is present only at relatively positive potentials in alkaline solutions. One of the surprising characteristics of Ag surfaces not previously discovered is that halide is chemisorbed at virtually all potentials, and not merely on the positive side as commonly believed. In fact, chemisorption of Cl^- , Br^- , and I^- is a one-electron redox process spanning the entire useful potential range; adsorption of I^- is so strong that it cannot be removed by reduction in aqueous electrolytes at pH 4 or 10. Cl and Br form a highly ordered Ag(111) ($\sqrt{3} \times \sqrt{3}$)R30° monoatomic layer, while I yields some of the same complex structures as are found in Ag deposition at iodine-pretreated Pt(111). (See References 52-54 and 56-58.) In other words, Ag is essentially always halide-covered in Cl^- , Br^- or I^- media, and is structurally reconstructed in I^- solutions.

K. Electrodeposition of Bi, Tl, Pb and Cu at Ag(111) Electrodes.

A step in the direction of understanding electroplating of non-noble substrates has been taken through studies of electrodeposition of Bi, Pb, Tl and Cu at Ag(111) from aqueous solutions (115).

Electrodeposition of Bi from trifluoroacetic acid (TFA) solutions onto Ag(111) under linear scan voltammetric conditions takes place in an underpotential deposition (UPD) peak followed by deposition of bulk Bi. Both stages involve substantial activation barriers. The Bi UPD layer is stable at open circuit, contains 0.55 Bi atoms per Ag surface atom, and is hexagonally close-packed in a $(2\frac{1}{3} \times 2\frac{1}{3})R30^\circ$ structure consisting of strip-shaped domains averaging $8.5\frac{1}{3}$ silver unit meshes in width. Electrodeposition of Pb onto Ag(111) from non-chemisorbing electrolytes such as acetate, TFA, and perchlorate gives three UPD peaks, while deposition from Cl^- , Br^- , or I^- media result in only one UPD peak. The Pb layers are unstable at open circuit. That is, Pb corrodes away in acidic aqueous solutions to yield an ordered layer of PbO , the structure of which is different for each halide electrolyte. Use of aprotic electrolytes to stabilize the Pb deposit should be explored in future work.

Electrodeposition of Tl from TFA electrolyte gives four UPD peaks. The electrodeposited Tl layer is unstable at open circuit, giving an ordered TlOH layer having a $(3\frac{1}{3} \times 3\frac{1}{3})R30^\circ$ structure.

Electrodeposition of Cu at Ag(111) gives no UPD peaks (Cu and Ag are chemically similar). The bulk Cu electrodeposit is stable at open circuit, and consists of monolayers of Cu which yield diffuse LEED patterns. That is, the Cu covers the surface evenly but has insufficient long-range order to yield interpretable LEED patterns.

L. Alkenoic Acids at Pt(111)

Studies of the electrochemical oxidation of a series of straight-chain terminal alkenoic acids adsorbed at a Pt(111) electrode surface from aqueous electrolyte have been conducted (138). Compounds adsorbed were: propenoic acid (acrylic acid, PPA); 3-butenic acid (vinylacetic acid, 3BTA); 4-pentenic acid (allylacetic acid, 4PTA); 6-heptenic acid (6HPA); and 10-undecenoic acid (10UDA). Vibrational spectra of adsorbed layers were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing densities were measured by use of Auger spectroscopy. Electrochemical

oxidation of each adsorbed layer was explored by means of cyclic voltammetry in aqueous inert electrolyte (KF/HF). As the analogous aliphatic acids are not chemisorbed at Pt under the same conditions, the alkenoic acids evidently adsorb at Pt(111) predominantly through the C=C double bond. Molecular packing densities indicate that the carboxylic acid moiety is in contact with the Pt surface only in the case of PPA. EELS spectra also indicate that the carboxylate groups (other than in PPA) are present as pendants. The carboxylic acid O-H stretching bands of most of the adsorbed acids are red-shifted and broadened, evidently due to extensive intermolecular hydrogen bonding; the exceptions are PPA, for which the interaction is primarily with the Pt surface, and 3BTA, for which intermolecular interaction between the carboxylic acid pendants is apparently prevented by steric considerations. The surface-attached carboxylic acid moieties react with KOH solution, leading to retention of K⁺ ions, detected by Auger spectroscopy, and to changes in the vibrational spectra indicative of carboxylate anions; reactivity toward KOH decreases with chain length. Adsorbed alkenoic acids at Pt(111) surfaces are stable in water and in vacuum. Oxidation of the adsorbed short-chain acids PPA and 3BTA proceeds to completion, forming CO₂ as the principal product. Oxidation of the adsorbed long-chain acids converts the C=C moiety to 2CO₂, and transforms the remainder of the molecule to an unadsorbed diacid (likely possibilities are malonic acid from 4PTA; glutaric acid from 6HPA; and heptane-1,7-dioic acid from 10UDA).

M. Multinitrogen Heteroaromatics at Pt(111):

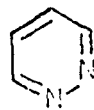
Surface electrochemical studies of several multi-nitrogen heteroaromatics and their carboxylic acid derivatives adsorbed at well defined Pt(111) electrode surfaces from aqueous solutions have been performed (139). The adsorbates studied include pyrazine (PZ), pyrimidine (PM), pyridazine (PD), 2-pyrazine carboxylic acid (PZCA), 2,3-pyrazinedicarboxylic acid (23PZDCA), 4-pyridazine carboxylic acid (4PDCA) and 1,3,5-triazine (TZ):



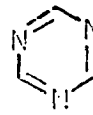
PZ



PM



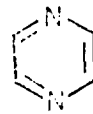
PD



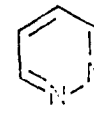
TZ



PZCA



23 PZDCA



4 PDCA

Packing densities (moles adsorbed per unit area) of each compound adsorbed from solution at controlled pH and electrode potential were measured by means of Auger spectroscopy. All of the above compounds except TZ adsorb strongly to Pt(111). Surface vibrational spectra of these adsorbed layers were obtained by electron energy-loss spectroscopy (EELS) and were compared with either vapor or condensed phase infrared (R) spectra of the parent compounds. The similarity of EELS and IR spectra indicate that the adsorbates retain their molecular structure unchanged as a result of adsorption. Adsorbed layers of these materials are stable in contact with aqueous fluoride solutions, and are stable also in vacuum. The adsorbed layer is electrochemically unreactive, and tends to passivate the Pt surface. Carboxylic acid substituents of these compounds interact with the Pt surface to an extent which depends upon the electrode potential. Long-range order is absent from the adsorbed layer, based upon LEED observations, although the Pt(111) surface remains ordered. The adsorbed molecules are attached to the surface primarily through the least hindered ring nitrogen atom, and are arranged in tilted-vertical orientation with the average ring-to-surface angles ranging from 73° to 86°, Figure 7.

N. Alkenols at Pt(111)

Studies of adsorption and electrochemical oxidation of a series of straight-chain terminal alkenols at a Pt(111) electrode surface have been conducted (141).. Vibrational spectra of each adsorbed layer were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing density in the adsorbed layer was measured by means of Auger electron spectroscopy. Substrate surface structure was monitored by use of LEED. Electrochemical oxidation of each adsorbed layer was explored by means of linear potential scan voltammetry in an inert aqueous electrolyte (KF/HF). Compounds studied are: 2-propen-1-ol (PPEOH, allyl alcohol); 3-buten-1-ol (BTEOH); 4-penten-1-ol (PTEOH); 5-hexen-1-ol (HXEOH); and 10-undecen-1-ol (UDEOH). Attachment to the surface is primarily through the C=C double bond, Figure 8. Regardless of chain length each chemisorbed alkenol molecule occupies an area similar to that of PPEOH. EELS spectra indicate that the C=C double bond is preserved in the adsorbed state. Evidently, the C=C axis is parallel to the Pt(111) surface, and the aliphatic chain is pendant. The -OH moiety is in contact with the Pt surface only in the case of PPEOH.

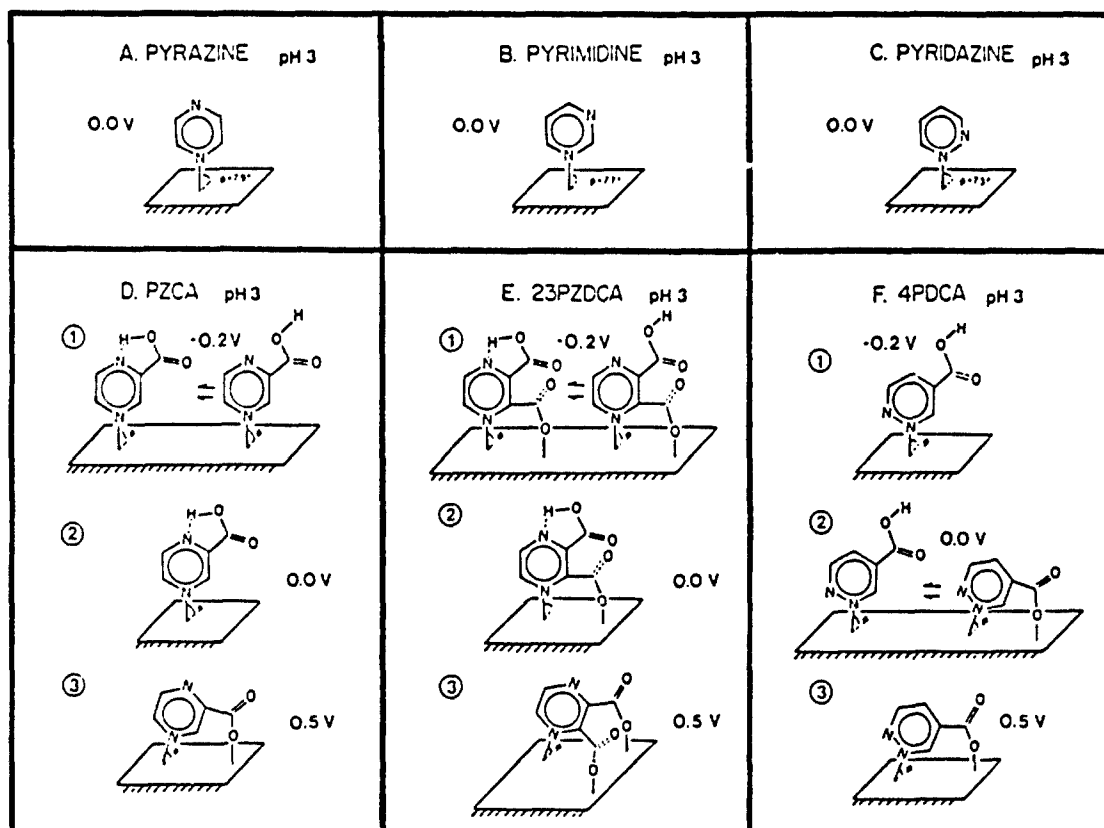


Figure 7: Structural models of adsorbed dinitrogen heteroaromatics (139). Values of θ based upon Auger data for adsorption from 1 mM adsorbate (pH 3) solution at 0.00 V are:

- | | |
|-------------------------------|------------------------------------|
| A. PZ ($\theta = 79^\circ$) | D. PZCA ($\theta = 86^\circ$) |
| B. PM ($\theta = 77^\circ$) | E. 23PZDCA ($\theta = 80^\circ$) |
| C. PD ($\theta = 73^\circ$) | F. 4PDCA ($\theta = 86^\circ$) |

An O-H stretching band is present only in the EELS spectrum of BTEOH; intermolecular hydrogen bonding (PTEOH, HXEOH, UDEOH) and interaction with the Pt surface (PPEOH) eliminate the O-H stretching bands of the other adsorbed terminal alkenols studied. Measurement of the average number of electrons, n_{ox} , required for catalytic electrochemical oxidation of an adsorbed molecule reveals that oxidation takes place primarily at the C=C double bond and one adjacent saturated carbon.

O. Alkenes at Pt(111)

Studies of the surface packing density, vibrational spectroscopy and electrochemical oxidation of a series of straight-chain terminal alkenes adsorbed from the vapor at a Pt(111) electrode surface have been completed (142). Compounds studied were: ethene (ETE), propene (PPE), 1-butene (BTE), 1-pentene (PTE), 1-hexene (HXE), 1-octene (OCE) and 1-decene (DCE). Vibrational spectra of the adsorbed layers were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing densities (nmol/cm^2) in the adsorbed layer were measured by use of Auger spectroscopy. Electrochemical oxidation of each adsorbed layer in aqueous inert electrolyte (KF/HF) was investigated by means of linear potential scan voltammetry. Attachment to the surface is through the C=C bond. Based upon molecular packing densities, the aliphatic chains are pendant; regardless of its chain length each chemisorbed alkene molecule occupies an area similar to that of chemisorbed PPE, Figure 9. The packing densities of ETE and PPE indicate an average orientation in which the C=C moiety is parallel to the Pt(111) surface. EELS spectra indicate that the C=C double bond is preserved in the adsorbed state of each 1-alkene studied. Measurement of the average number of electrons, n_{ox} , required to electro-oxidatively desorb an adsorbed 1-alkene molecule reveals that the catalytic electrochemical oxidation process involves primarily the C=C double bond and one adjacent saturated carbon atom.

Figure 8: Structural models of adsorbed terminal alkenols at Pt(111).

- A. PPEOH
- B. BTEOH
- C. PTEOH
- D. HXEOH
- E. UDEOH

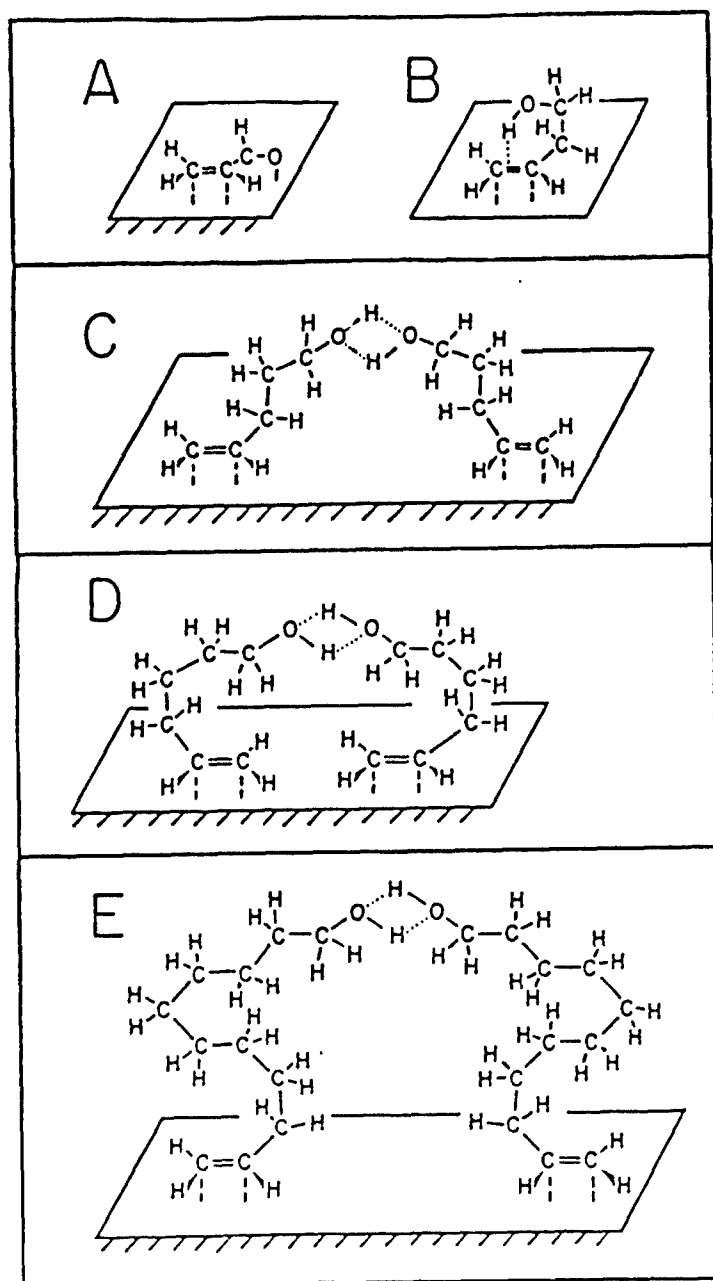
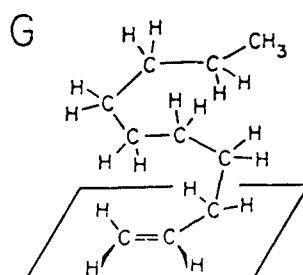
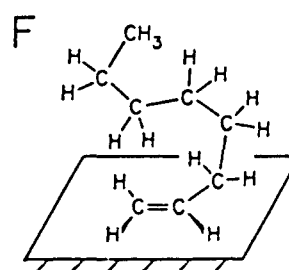
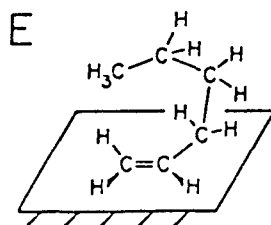
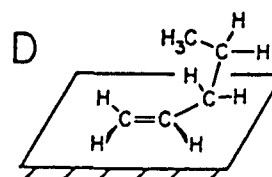
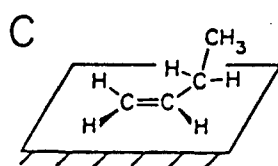
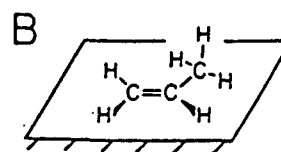
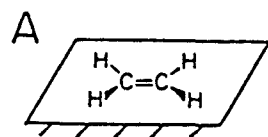


Figure 9: Structural models of adsorbed 1-alkenes at Pt(111):

- | | | | |
|----|-----|----|-----|
| A. | ETE | D. | PTE |
| B. | PPE | E. | XHE |
| C. | BTE | F. | OCE |
| | | G. | DCE |



P. Comparison of EELS and IR Spectra:

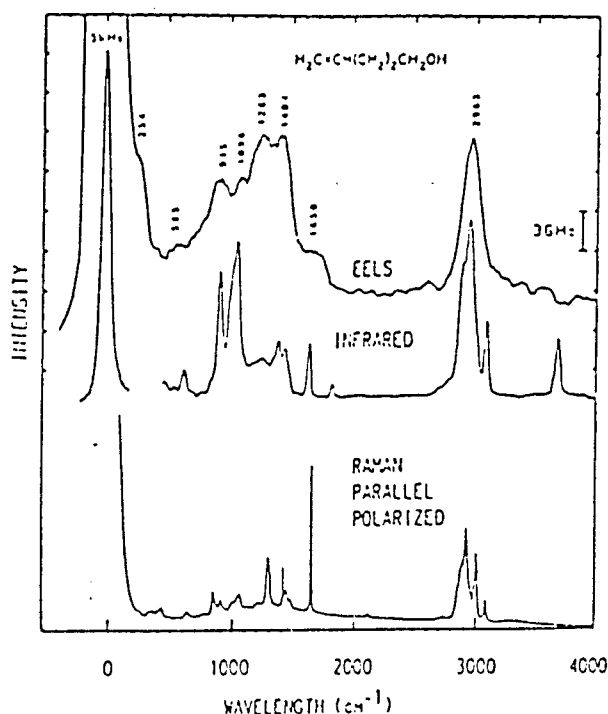
EELS spectra obtained for the adsorbed species formed from aqueous electrolytes at Pt(111) electrode surfaces have been compared with the IR and Raman spectra of the unadsorbed compounds in order to reveal the changes in vibrational spectra resulting from chemisorption of various important functional groups, and to explore the differences in vibrational absorptivities between EELS spectra of adsorbed species and IR and Raman spectra of the corresponding unadsorbed compounds (146). Of particular interest are the variations in EELS vibrational frequency, band width and absorptivity due to bonding with the surface, intermolecular interactions of adsorbed molecules and changes in adsorbate molecular orientation. The influence of surface bonding on the EELS spectrum of a functional group was explored through studies of phenol (PL), phenol- d_6 (PLD6), benzyl alcohol (BZOH), catechol (CT), benzoic acid (BA), 2-picolinic acid (PA), 2,6-pyridine dicarboxylic acid (26PDCA), and propenoic acid (PPEA). The aromatic ring of adsorbed PL, POD6, BZA, CT, BA, PA and 26PDCA is oriented parallel to the Pt(111) surface. The resulting strong interactions affect the frequencies and relative intensities of the EELS bands: weak CH stretching modes; a large CC stretching band ($1600\text{--}1650\text{ cm}^{-1}$), and weak CH bending ($700\text{--}800\text{ cm}^{-1}$).

The carboxylic acid moieties of BA and PA interact strongly with the Pt surface, while those of 26PDCA do so only when adsorbed at relatively positive electrode potentials. O-H stretching and bending are absent from the EELS spectra of adsorbed PL, BZOH and CT, perhaps due to dissociation of the hydroxyl hydrogen during adsorption of the molecule. Adsorption of alkenes at Pt(111) from solution preserves the characteristic C=C stretching band near 1650 cm^{-1} ; examples are: PPEA; 1-hexene (HXE); propenol (PPEOH); 4-pentenol (PTEOH), Figure 10; and *cis*-2-butene-1,4-diol (CBED); adsorption of ethene, propene and butene from vacuum at room temperature has been reported to result in loss of double-bond character. Adsorption of propynol (PPYOH) lowers the frequency of the $\text{C}\equiv\text{C}$ triple-bond to approximately that of a double-bond. EELS spectra of adsorbed pyridine (PY), 2-methylpyridine (2MPY) and 2,6-dimethylpyridine (26DMPY) were examined in order to contrast the vibrational behavior of adsorbates having the aromatic ring perpendicular to the Pt surface (PY and 2MPY), giving rise to strong perturbation of the vibrational spectra or parallel (26DMPY), leading to limited perturbation of the vibrational spectra. Compounds for which the

surface interaction is limited primarily to bonding of a single sulfur atom were studied in order to observe the vibrational behavior of a comparatively unperturbed pendant ring or chain: thiophenol (TP); benzylmercaptan (BM); cysteine (CYS); and thiophene (TPE). The expected lack of perturbation was found, making TP, BM and CYS particularly suitable reference compounds for surface vibrational studies of aromatic rings and amino acids.

In contrast, L-phenylalanine (PHE) interacts with the Pt(111) surface through the phenyl ring as well as the amino acid functionality. In general, chemisorption and intra-layer intermolecular interaction both lower the surface vibrational frequencies (EELS) and incidentally affect peak amplitudes. Orientation affects peak amplitudes and incidentally affects frequencies insofar as a change in orientation is accompanied by a change in mode of surface bonding. Surface roughness leads to a scrambling of adsorbed states which affects bandwidths, chemical/electrochemical reactivities, and in turn the frequencies and amplitudes of EELS peaks. Specific findings and conclusions are presented for each compound and correlated.

Figure 10: EELS, IR and Raman spectra of 4-pentene-1-ol (PTEOH). EELS: PTEOH adsorbed at Pt(111) from 1 mM aqueous PTEOH in 10 mM KF (pH 3) at -0.1 V (141). IR: PTEOH vapor at 200°C (Sadtler standard spectrum). Raman: PTEOH liquid (Thermodynamics Res. Center Spectra Data, Texas A&M University).



Q. Imaging Metal Surface Atomic Structure (135,140,154).

Measurements of the complete angular distributions of low energy Auger electrons emitted from well-defined single-crystal surfaces, as illustrated in Figure 11, have led to

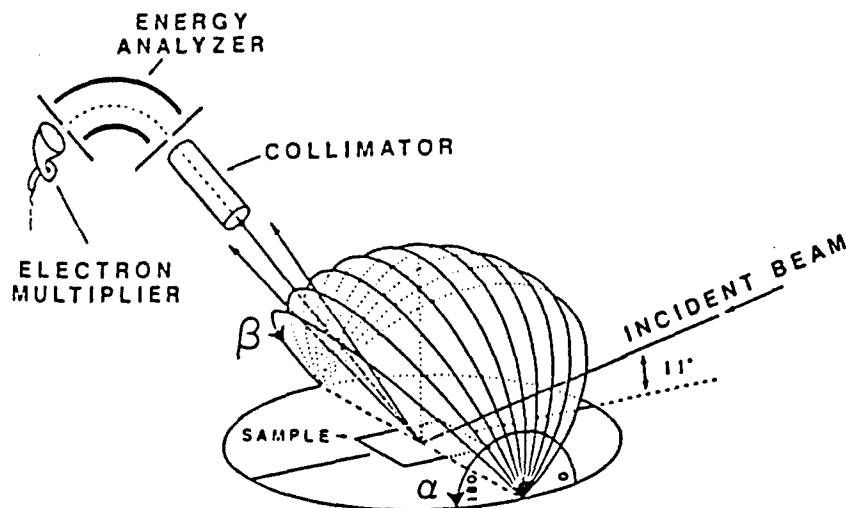


Figure 11 ADAM angular distributions are measured vs. the angular coordinates of the detector (α and β). Auger electron emission is stimulated by a fixed grazing incidence electron gun. Auger electrons emitted from the sample (also fixed) along trajectories selected by the moving analyzer must pass through angle- and energy-resolving optics before being amplified, counted, and recorded.

the discovery that the distributions contain silhouettes of surface atoms backlit by emission from atoms deeper in the solid. Theoretical simulations of Auger electron angular distributions based upon atomic point emitters and spherical atomic scatterers are in close agreement with these experimental results. In view of the definitive results obtained and the straightforward agreement between theory and experiment, angular distribution Auger microscopy (ADAM) is useful for direct imaging of atomic structure, and for fundamental studies of the interaction of electrons with matter. Usefulness of ADAM has been demonstrated by studies of Pt and Ag single crystals, and of thin films of Ag produced by electro-deposition (135,154).

R. Some Implications of These Results

Let us now spend a few moments to consider some of the theoretical and practical implications of the results which have been gathered.

Of course, a very useful implication of the remarkable lack of influence of vacuum and the weak electron beams employed in our electron spectroscopy experiments is that such surface analysis procedures are demonstrated to be applicable to analysis of electrode surfaces. These UHV techniques offer enormous advantages of sensitivity, generality, directness, accuracy, definitiveness, and so forth. This does not mean that we are turning away from the "wet" methods such as thin-layer electrochemistry, voltammetry, coulometry, impedance and so on, which continue to be essential, nor have we ever done so in the past. The success of these techniques also allows study for the first time at electrode surfaces of the behavior of compounds which do not have any particular electrochemical reactivity. We are now prepared to study any chemisorbed compound in any practical amount. Weakly adsorbed compounds of course require other methods.

A benefit of the observed similarity between EELS spectra of adsorbed compounds and IR spectra of unadsorbed compounds is that the extensive IR literature will greatly facilitate assignment of the EELS spectra and identification of adsorbed species. EELS has produced definitive spectra of all of the chemisorbed compounds we have studied thus far. Sensitivity is excellent, although resolution is moderate. The full frequency range is covered from far IR to near IR. Beam damage is generally negligible. Reproducibility in our experiments is excellent. The correlation between EELS spectra and electrochemical conditions is remarkably close. Nevertheless, EELS is not a stand-alone technique; its usefulness increases when it is combined with other definitive techniques and with reproducibly prepared samples.

Confirmation of the thin-layer electrochemical measurements of hydroquinone and related packing densities by Auger spectroscopy has the advantage of strengthening confidence in electrochemical and vacuum measurements. Comparison of data can also test the accuracy of calibration of the various methods. Differences between polycrystalline TLE results and single-crystal UHV results are useful in understanding the role of surface structure in catalytic processes. UHV studies of polycrystalline surfaces also contribute to understanding of this matter.

Comparison of electrochemical reactivity, packing density, stoichiometry and vibrational spectroscopy at electrochemically-cycled surfaces versus UHV annealed surfaces under otherwise identical conditions consistently reveals major differences in behavior. Such information is a valuable source of clues as to the role of surface structure and of adsorbed species in surface chemistry, catalysis and materials behavior. It is also a warning concerning the risks of surface spectroscopy and chemistry projects which ignore surface characterization.

Comparisons such as the amino acid studies at Pt(111) and Pt(100) of the influence of crystal planes on adsorption and electrochemical reactivity are a source of previously unavailable, essential information concerning the nature of adsorbed intermediates and the factors controlling reaction rates and product distribution.

Investigations of NA under conditions of potential-dependent and pH-dependent adsorption have yielded a remarkably definitive and unusual look into the interactions between a surface, an adsorbed layer and a solution. These observations are proving to be general, as noted from the trends consistently displayed by a variety of compounds. Surface electrochemistry and acid-base chemistry will never be the same again. LEED studies of PYR and other organic adsorbates at electrodes reveal some intriguing characteristics of the close-packed, oriented but incommensurate and presumably undulating layers. The cyclic voltammetry of adsorbed pyridine and benzoic acid reveals the remarkable differences in electrochemical reactivity of the N-bonded pyridine molecule and the pi-bonded benzoic acid (or other horizontally oriented benzene derivatives).

Studies of the layers formed by adsorption from ionic solutions such as sulfide are an essential part of the understanding of electrodes and electrical double-layers. They are also of importance in connection with passivation, metal coating and electroplating behavior. Surface structure studies and theories of surface valency will benefit from this new knowledge.

Alcohols are of great interest in connection with fuel cell behavior. Unsaturated alcohols readily provide insights into the behavior of aqueous organic solutions. Electro-oxidation rates, mechanisms and products are accessible for alcohol solutions. Studies of the neat alcohols are one of the first instances of study of pure liquids in contact with well-defined metallic surfaces.

Electropolymerization studies at well-defined surfaces by use of the techniques employed in our work will add a useful bit of information concerning the nature of the films: stoichiometry, mode of attachment, and molecular structure from Auger, EELS and surface infrared spectroscopy.

Studies of non-noble metals, whether silver, ferrous alloys, or virtually any other element or combination, often much easier to achieve than those of the difficult metal platinum, will broaden and deepen the understanding gained from such experiments. Electrodeposition studies at the level of atoms and molecules are vital to microcircuit fabrication and preparation of metal doped catalysts.

While many of our recent studies have focused on a few compounds, we note that there is also theoretical and practical benefit in studying families of compounds spanning the various possible chemical characteristics, thus allowing the opportunity to discover phenomena and trends which might be missed by investigations of only a small set of similar compounds.

Clearly, the measurement of low-energy Auger electron angular distributions (the ADAM method) will yield valuable evidence regarding the structures of crystalline surfaces, atomic layers, ionic layers, molecular layers, alloys and thin-films of importance in the entire range of chemical, physical and biological sciences and engineering.

III. PUBLICATIONS

** Denotes Work Supported by Air Force Office of Scientific Research

1. "Electrochemistry in Thin Layers of Solution", Ph.D. Thesis, California Institute of Technology, 1967, (University Microfilms, Ann Arbor, Michigan, document no. 67-6006).
2. New Electrodes for Chronopotentiometry in Thin Layers of Solution. Arthur T. Hubbard and Fred C. Anson, *Anal. Chem.*, **36**, 723 (1964).
3. Thin Layer Chronopotentiometric Determination of Reactants Adsorbed on Platinum Electrodes. Arthur T. Hubbard and Fred C. Anson, *J. Electroanal. Chem.*, **9**, 163 (1965).
4. Linear Potential Sweep Voltammetry in Thin Layers of Solution. Arthur T. Hubbard and Fred C. Anson, *Anal. Chem.*, **38**, 58 (1966).
5. Further Study of the Iodide-Iodine Couple at Platinum Electrodes by Thin Layer Electrochemistry. Arthur T. Hubbard, Robert A. Osteryoung and Fred C. Anson, *Anal. Chem.*, **38**, 692 (1966).
6. Determination of Adsorbed Cobalt and Iron Ethylenedinitrilotetraacetate Complexes on Platinum Electrodes by Thin Layer Electrochemistry. Arthur T. Hubbard and Fred C. Anson, *Anal. Chem.*, **38**, 1601 (1966).
7. Study of the Electrochemistry of Chloride and Bromide Complexes of Platinum (II) and (IV) by Thin Layer Electrochemistry. Arthur T. Hubbard and Fred C. Anson, *Anal. Chem.*, **38**, 1887 (1966).
8. A New Mercury Electrode for Thin Layer Electrochemistry. Arthur T. Hubbard and Fred C. Anson, *Anal. Chem.*, **40**, 615 (1968).
9. Electrochemical and Spectral Studies of Dimeric Iron (III) Complexes. Harvey J. Schugar, Arthur T. Hubbard, Fred C. Anson and Harry B. Gray, *J. Amer. Chem. Soc.*, **91**, 71 (1969).
10. Thin Layer Electrochemistry in Molten Salt Solutions. Louis P. Zajicek and Arthur T. Hubbard, *J. Electrochem. Soc.*, **116**, 80C (1969).
11. Study of the Kinetics of Electrochemical Reactions by Thin-Layer Voltammetry. I. Theory. Arthur T. Hubbard, *J. Electroanal. Chem.*, **22**, 165 (1969).
12. Study of the Kinetics of Electrochemical Reactions by Thin-Layer Voltammetry. II. Electro-Oxidation of Platinum (II) Complexes. Joseph P. Cushing and Arthur T. Hubbard, *J. Electroanal. Chem.*, **23**, 183 (1969).

13. The Theory and Practice of Electrochemistry with Thin Layer Cells.
Arthur T. Hubbard and Fred C. Anson, *Electroanal. Chem.*, **4**, 129 (1970).
14. Study of the Kinetics of Electrochemical Reactions by Thin Layer Voltammetry.
III. Electroreduction of the Chloride Complexes of Platinum (II) and (IV).
Arthur L. Y. Lau and Arthur T. Hubbard, *J. Electroanal. Chem.*, **24**, 237 (1970).
15. Thin Layer Electrochemistry. Minimization of Uncompensated Resistance.
G. M. Tom and A. T. Hubbard, *Anal. Chem.*, **43**, 671 (1971).
16. Study of the Kinetics of Electrochemical Reactions by Thin Layer Voltammetry.
IV. The Influence of Chemisorbed Species on the Reactions of Platinum
Complexes at Platinum Electrodes. Arthur L. Y. Lau and Arthur T. Hubbard,
J. Electroanal. Chem., **33**, 77 (1971).
17. Halide-Bridged Electrode Reactions of Platinum Complexes Containing
Unsaturated Ligands. Chiu-Nan Lai and Arthur T. Hubbard, *Inorg. Chem.*,
11, 2081 (1972).
18. Electrochemistry of Chemisorbed Molecules. I. Reactants Connected to
Electrodes through Olefinic Substituents. Ross F. Lane and Arthur T. Hubbard,
J. Phys. Chem., **77**(11), 1401 (1973).
19. Electrochemistry of Chemisorbed Molecules. II. The Influence of Charged
Chemisorbed Molecules on the Electrode Reactions of Platinum Complexes.
Ross F. Lane and Arthur T. Hubbard, *J. Phys. Chem.*, **77**(11), 1411 (1973).
20. Electrochemistry in Thin Layers of Solution. Arthur T. Hubbard, *CRC Crit.
Rev. of Anal. Chem.*, **3**, 201 (1973).
21. Quantum Mechanical Description of Electrode Reactions. I. Extended-Huckel
Molecular Orbital Treatment of the Halide-Bridged Electrode Reactions of
Platinum Complexes. Chiu-Nan Lai and Arthur T. Hubbard, *Inorg. Chem.*, **13**,
1199 (1974).
22. Investigation of Electrode Surfaces by Means of Combined Electrochemical and
Electron-Scattering Techniques. Arthur T. Hubbard, Roy M. Ishikawa and
James A. Schoeffel. Symposium on Electrocatalysis, The Electrochemical
Society (U.S.A.), San Francisco, California, 1974.
23. Characterization of Electrode Surfaces by Means of Thin Layer Electrochemistry
and LEED. Arthur T. Hubbard, Roy M. Ishikawa and James A. Schoeffel.
Symposium on Characterization of Adsorbed Species in Catalytic Reactions,
Chemical Institute of Canada, Ottawa, Canada, 1974.

24. Electrochemistry of Chemisorbed Molecules. III. Determination of the Oxidation State of Halides Chemisorbed on Platinum. Reactivity and Catalytic Properties of Adsorbed Species. Ross F. Lane and Arthur T. Hubbard, *J. Phys. Chem.*, **79**, 808 (1975).
25. Study of Platinum Electrodes by Means of Thin layer Electrochemistry and Low Energy Electron Diffraction. Part I. Electrode Surface Structure After Exposure to Water and Aqueous Electrolytes. Roy M. Ishikawa and Arthur T. Hubbard, *J. Electroanal. Chem.*, **69**, 317 (1976).
26. Quantum Mechanical Description of Electrode Reactions. Part II. Treatment of Compact Layer Structure at Platinum Electrodes by Means of the Extended Huckel Molecular Orbital Method: Pt(111) Surfaces. Marzio A. Leban and Arthur T. Hubbard, *J. Electroanal. Chem.*, **74**, 253 (1976).
27. Differential Double Pulse Voltammetry at Chemically Modified Platinum Electrodes for in vivo Determination of Catecholamines. Ross R. Lane and Arthur T. Hubbard, *Anal. Chem.*, **48**, 1287 (1976).
28. Brain Catecholamines: Detection in vivo by Means of Differential Pulse Voltammetry at Surface-Modified Pt Electrodes. Ross F. Lane, Arthur T. Hubbard, Kenneth Fukunaga and Robert J. Blanchard, *J. Brain Res.*, **114**, 346 (1976).
29. Electrochemistry of Chemisorbed Molecules. 5. Role of Non-Aqueous Solvents in Ligand-Bridged Electrochemical Interconversion of Platinum Complexes. Ross F. Lane and Arthur T. Hubbard, *J. Phys. Chem.*, **81**, 734 (1977).
30. Quantitative Elemental Analysis of Substituted Hydrocarbon Monolayers on Platinum by Auger Electron Spectroscopy with Electrochemical Calibration. James A. Schoeffel and Arthur T. Hubbard, *Anal. Chem.*, **49**, 2330 (1977).
31. Study of Platinum Electrodes by Means of Electrochemistry and Low-Energy Electron Diffraction. Part II. Comparison of the Electrochemical Activity of Pt(100) and Pt(111) Surfaces. Arthur T. Hubbard, Roy M. Ishikawa, and James Y. Katekaru, *J. Electroanal. Chem.*, **86**, 271 (1978).
32. Brain Dopaminergic Neurons: In vivo Electrochemical Information Concerning Storage, Metabolism and Release Processes. Ross F. Lane, Arthur T. Hubbard and Charles D. Blaha, *Bioelectrochem. Bioenerg.*, **5**, 504 (1978).

33. Application of Semidifferential Electroanalysis to Studies of Neurotransmitters in the Central Nervous System. Ross F. Lane, Arthur T. Hubbard and Charles D. Blaha, *J. Electroanal. Chem.*, **95**, 117 (1979).
34. In Vivo Voltammetric Monitoring of Dopamine Release and Catabolism in the Rat Striatum. In, "Catecholamines: Basic and Clinical Frontiers", E. Usdin, ed., Oxford Pergamon Press, volume 1, pp 883ff, 1979.
35. LEED and Electrochemistry of Iodine on Pt(100) and Pt(111) Single-Crystal Surfaces. Thomas E. Felter and Arthur T. Hubbard, *J. Electroanal. Chem.*, **100**, 473 (1979).
36. Electrochemistry of Well-Defined Surfaces. Arthur T. Hubbard, *Acc. Chem. Res.*, **13**, 177 (1980).
37. Electrochemistry of Single-Crystal Surfaces. Arthur T. Hubbard, *J. Vac. Sci. Technol.*, **17**, 49 (1980).
38. Superlattices Formed by Interaction of Hydrogen Iodide with Pt(100) and Pt(111) Studied by LEED, Auger, and Thermal Desorption Mass Spectroscopy. Gerald A. Garwood, Jr., and Arthur T. Hubbard, *Surface Sci.*, **92**, 617 (1980).
39. Electrochemical Hydrogenation of Ethylene at Well-Defined Pt(100) and Pt(111) Surfaces. Arthur T. Hubbard, Mark A. Young and James A. Schoeffel, *J. Electroanal. Chem.*, **114**, 273 (1980).
40. A Survey of Factors Influencing the Stability of Organic Functional Groups Attached to Platinum Electrodes. John L. Stickney, Manuel P. Soriaga, Arthur T. Hubbard and Stanley E. Anderson, *J. Electroanal. Chem.*, **125**, 73 (1981).
41. Superlattices Formed by Interaction of Hydrogen Bromide and Hydrogen Chloride with Pt(100) and Pt(111) Studied by LEED, Auger, and Thermal Desorption Mass Spectroscopy. Gerald A. Garwood, Jr., and Arthur T. Hubbard, *Surf. Sci.*, **112**, 281 (1982).
42. Superlattices Formed by Interaction of Polar Solvents with Pt(111) Surfaces Studied by LEED, Auger Spectroscopy and Thermal Desorption Mass Spectroscopy. Gerald A. Garwood, Jr., and Arthur T. Hubbard, *Surf. Sci.*, **118**, 223 (1982).
43. Determination of the Orientation of Adsorbed Molecules at Solid-Liquid Inter-
** faces by Thin-Layer Electrochemistry: Aromatic Compounds at Platinum Electrodes. Manuel P. Soriaga and Arthur T. Hubbard, *J. Amer. Chem. Soc.*, **104**, 2735 (1982).

44. Determination of the Orientation of Aromatic Molecules Adsorbed on Platinum
** Electrodes: The Influence of Iodide, a Surface Active Anion. Manuel P. Soriaga and Arthur T. Hubbard, *J. Amer. Chem. Soc.*, 104, 2742 (1982).
45. Structure and Composition of Adsorbed Layer Formed by Sequential Exposure of Pt(100) and Pt(111) to Pairs of Compounds: Solvents and Electrolytic Substances. James. Y. Katekaru, John Hershberger, Gerald A. Garwood, Jr., and Arthur T. Hubbard, *Surf. Sci.*, 121, 396 (1982).
46. Superlattices Formed by Interaction of Iodine, Water and Oxygen with the (111) Plane of a Face-Centered Cubic Stainless Steel Single-Crystal. Jesse B. Lumsden, Gerald A. Garwood, Jr., and Arthur T. Hubbard, *Surf. Sci.*, 121, 1524 (1982).
47. Determination of the Orientation of Aromatic Molecules Adsorbed on Platinum
** Electrodes: The Effect of Solute Concentration. Manuel P. Soriaga and Arthur T. Hubbard, *J. Amer. Chem. Soc.*, 104, 3397 (1982).
48. Theoretical Determination of the Structure on Acetylene on Pt(111). Alfred B. Anderson and Arthur T. Hubbard, *Surf. Sci.*, 99, 384 (1982).
49. Orientational Transitions of Aromatic Molecules Adsorbed on Platinum
** Electrodes. Manuel P. Soriaga, Peggy H. Wilson, Arthur T. Hubbard and Clifford S. Benton, *J. Electroanal. Chem.*, 142, 317 (1982).
50. The Effect of Orientation of Adsorbed Intermediates on the Electrochemical
** Oxidation of Adsorbed Aromatic Compounds. Manuel P. Soriaga, John L. Stickney and Arthur T. Hubbard, *J. Mol. Catal.*, 21, 211 (1983).
51. Electrochemical Oxidation of Aromatic Compounds Adsorbed on Platinum
** Electrodes: The Influence of Molecular Orientation. Manuel P. Soriaga, John L. Stickney and Arthur T. Hubbard, *J. Electroanal. Chem.*, 144, 207 (1983).
52. Electrodeposition on a Well-Defined Surface: Silver on Pt(111)($\sqrt{7} \times \sqrt{7}$)-I.
** Arthur T. Hubbard, John L. Stickney, Stephen D. Rosasco, Manuel P. Soriaga, and Dian Song, *J. Electroanal. Chem.*, 150, 165 (1983).
53. Electrochemistry of Chemisorbed Molecules. 4. The Effect of Chirality
** on the Orientation and Electrochemical Oxidation of l- and dl-DOPA. Victor K. F. Chia, Manuel P. Soriaga, Arthur T. Hubbard and Stanley E. Anderson, *J. Phys. Chem.*, 87, 232 (1983).

54. Superlattices Formed by Electrodeposition of Silver on Iodine-Pretreated
** Pt(111). Studies by LEED, Auger Spectroscopy and Electrochemistry.
John L. Stickney, Stephen D. Rosasco, Dian Song, Manuel P. Soriaga and
Arthur T. Hubbard, *Surf. Sci.*, **130**, 326 (1983).
55. Electrodeposition of Copper on Platinum (111) Surfaces Pretreated with
** Iodine. Studies by LEED, Auger Spectroscopy and Electrochemistry. John L.
Stickney, Stephen D. Rosasco and Arthur T. Hubbard, *J. Electrochem. Soc.*,
131, 260 (1984).
56. Electrodeposition of Silver on Pt(100) Surfaces Containing Iodine Adlattices.
** Studies by Low-Energy Electron Diffraction, Auger Spectroscopy, and Thermal
Desorption. John L. Stickney, Stephen D. Rosasco, Bruce C. Schardt and
Arthur T. Hubbard, *J. Phys. Chem.*, **88**, 251 (1984).
57. Preparation of Well-Defined Surfaces under Atmospheric Conditions. Studies
** by Electrochemistry and LEED of Pt(100) Pretreated with Iodine. Andrzej
Wieckowski, Stephen D. Rosasco, Bruce C. Schardt, John L. Stickney and Arthur
T. Hubbard, *Inorg. Chem.*, **23**, 565 (1984).
58. Preparation of Well-Defined Surfaces at Atmospheric Pressure: Studies of
** Structural Transformations of Iodine Adlattices on Pt(111) by LEED and
Electrochemistry. Andrzej Wieckowski, Bruce C. Schardt, Stephen D. Rosasco,
John L. Stickney and Arthur T. Hubbard, *Surf. Sci.*, **146**, 115 (1984).
59. Orientation of Aromatic Molecules Adsorbed on Pt Electrodes: The Effect of
** Temperature. Manuel P. Soriaga, James H. White and Arthur T. Hubbard, *J.*
Phys. Chem., **87**, 3048 (1983).
60. Influence of Temperature on the Electrocatalytic Oxidation of Aromatic
** Compounds Adsorbed on Platinum. Manuel P. Soriaga and Arthur T. Hubbard,
J. Phys. Chem., **88**, 1758 (1984).
61. Electrode Reactions of Oriented Chemisorbed Molecules: The Effect of
** Temperature on Reversible Redox, Irreversible Oxidation and Reductive Desul-
furization. Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*,
159, 101 (1984).
62. Formation of Vertically-Oriented Aromatic Molecules Chemisorbed on Platinum
** Electrodes: The Effect of Surface Pretreatment with Flat Oriented Intermed-
iates. Manuel P. Soriaga and Arthur T. Hubbard, *J. Phys. Chem.*, **88**, 1089
(1984).

63. The Orientation and Electrochemical Oxidation of Hydroquinone Chemisorbed
** on Platinum Electrodes in Various Weakly Surface Active Supporting
Electrolytes. Manuel P. Soriaga, Victor K. F. Chia, James H. White,
Dian Song and Arthur T. Hubbard, *J. Electroanal. Chem.*, 162, 43 (1984).
64. Adsorption of Aromatic Compounds at Platinum Electrodes: A Comparative
** Study Illustrating the Deficiencies of Adsorption Measurements Based on
Hydrogen Codeposition or Anodic Oxidation. Manuel P. Soriaga and Arthur
T. Hubbard, *J. Electroanal. Chem.*, 167, 79 (1984).
65. The Adsorption, Orientation, and Electrochemical Oxidation of Hydroquinone
** at Smooth Platinum Electrodes: The Effect of Electrode Potential. Victor
K. F. Chia, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*,
167, 97 (1984).
66. Adsorption and Orientation of Aromatic Compounds at Smooth Polycrystalline
** Pt Electrodes. The Effect of Halide Electrolytes. Manuel P. Soriaga,
James H. White, Dian Song and Arthur T. Hubbard, *J. Electroanal. Chem.*, 171,
359 (1984).
67. Studies of Electrodeposition of Silver on Iodine Pretreated Platinum Step-
** Terrace Surface: Pt(S)[6(111)x(111)]. Tihomir Solomun, Bruce C. Schardt,
Stephen D. Rosasco, Andrzej Wieckowski, John L. Stickney and Arthur T.
Hubbard, *J. Electroanal. Chem.*, 176, 309 (1984).
68. Demonstration of the Stability of the van der Waals Surface (0001) of MoSe₂
** by LEED and Electrochemistry. John L. Stickney, Stephen D. Rosasco, Bruce C.
Schardt, Tihomir Solomun, Arthur T. Hubbard and Bruce A. Parkinson, *Surf.
Sci.*, 136, 15 (1984).
69. Atomic Structure at Electrode Surfaces. Gerald A. Garwood, Jr., and Arthur
T. Hubbard. In, "Proceedings of the Symposium on Advances in Materials
Characterization", D. R. Rossington, R. A. Condrate and R. L. Snyder, Eds.,
Plenum Press, New York, 1983, volume 15, pp 91-108.
70. Ligand (Adsorbate) Substitutions at Metal Surfaces: Aromatic Compounds and
** Halides at Smooth Polycrystalline Platinum Electrodes. Manuel P. Soriaga,
James H. White, Dian Song and Arthur T. Hubbard, *J. Phys. Chem.*, 88, 2285
(1984).

71. Adsorption and Orientation of Hydroquinone and Hydroquinone Sulfonate at
** Platinum Electrodes. Studies by Thin-Layer Electrochemistry, LEED, Auger
and Infrared Spectroscopy. Victor K.F. Chia, John L. Stickney, Manuel P.
Soriaga, Stephen D. Rosasco, Ghaleb N. Salaita, Arthur T. Hubbard, Jay B.
Benziger and K. W. Peter Pang, *J. Electroanal. Chem.*, **163**, 407 (1984).
72. Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes.
** Adsorption, Orientation, and Mode of Binding of Aromatic and Quinonoid
Compounds. Manuel P. Soriaga, Elizabeth Binamira-Soriaga, Arthur T.
Hubbard, Jay B. Benziger and K. W. Peter Pang, *Inorg. Chem.*, **24**, 65 (1985).
73. Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes.
** Surface Chemical Reactivity of Aromatic and Quinonoid Compounds Adsorbed in
Specific Orientational States. Manuel P. Soriaga, James H. White, Victor
K.F. Chia, Dian Song, Peter O. Arrhenius and Arthur T. Hubbard, *Inorg.
Chem.*, **24**, 73 (1985).
74. Iodine Adsorption on a Stepped Platinum Surface Pt[6(111)x(111)].
Tihomir Solomun, Andrzej Wieckowski, Stephen D. Rosasco and Arthur T.
Hubbard, *Surf. Sci.*, **147**, 241 (1984).
75. A Comparison of Gas Phase and Electrochemical Hydrogenation of Ethylene at
** Platinum Surfaces. Andrzej Wieckowski, Stephen D. Rosasco, Ghaleb N. Salaita,
Arthur T. Hubbard, Brian Bent, Francisco Zaera and Gabor A. Somorjai, *J.
Amer. Chem. Soc.*, **107**, 5910 (1985).
76. Ordered Ionic Layers formed on Pt(111) from Aqueous Solutions. John L.
** Stickney, Stephen D. Rosasco, Ghaleb N. Salaita and Arthur T. Hubbard,
Langmuir, **1**, 66 (1985).
77. Electrochemical Processes at Well-Defined Surfaces. Arthur T. Hubbard,
** John L. Stickney, Manuel P. Soriaga, Victor K.F. Chia, Stephen D. Rosasco,
Bruce C. Schardt, Tihomir Solomun, Dian Song, James H. White, and Andrzej
Wieckowski. Proceedings of the Sixth Australian Electrochemistry Conference,
J. Electroanal. Chem., **168**, 43 (1984).
78. Orientation of Hydroquinone and Benzoquinone on Platinum Electrodes:
** Studies by Reflection-Adsorption Infrared Spectroscopy. K. W. Peter Pang,
Jay B. Benziger, Manuel P. Soriaga and Arthur T. Hubbard, *J. Phys. Chem.*, **88**,
4583 (1984).
79. Effect of Surface Roughness on Adsorption, Orientation and Anodic Oxidation of
** Hydroquinone at Platinum Electrodes. James H. White, Manuel P. Soriaga and
Arthur T. Hubbard, *J. Electroanal. Chem.*, **177**, 89 (1984).

80. Adsorbate Exchange and Insertion Reactions at Metal Surfaces: Hydroquinone and Naphthohydroquinone at Smooth Polycrystalline Platinum in Aqueous Solutions. Manuel P. Soriaga, Dian Song and Arthur T. Hubbard, *J. Phys. Chem.*, **89**, 285 (1985).
**
81. Environmentally Produced Films on Stainless Steel Single-Crystal Surfaces. David A. Harrington, Andrzej Wieckowski, Stephen D. Rosasco, Ghaleb N. Salaita, Arthur T. Hubbard and Jesse B. Lumsden, Proceedings of the Pourbaix Symposium, The Electrochemical Society, Inc., Princeton, New Jersey (1984).
82. Competitive Chemisorption from Binary Surfactant Mixtures at Solid-Liquid Interfaces: Hydroquinone and Naphthohydroquinone at Smooth Polycrystalline Platinum Electrodes in Aqueous Solutions. Manuel P. Soriaga, Dian Song, Donald C. Zapien and Arthur T. Hubbard, *Langmuir*, **1**, 123 (1985).
**
83. Films Formed on Well-Defined Stainless Steel Single-Crystal Surfaces in Oxygen and Water: Studies of the (111) Plane by LEED, Auger, and XPS. David A. Harrington, Andrzej Wieckowski, Stephen D. Rosasco, Bruce C. Schardt, Ghaleb N. Salaita, Jesse B. Lumsden and Arthur T. Hubbard, *Corrosion Sci.*, **25**, 849 (1985).
84. The Adsorption and Orientation of Aromatic Compounds at Smooth Polycrystalline Platinum Electrodes. The Effects of Low-Level Surface Active Impurities. Dian Song, Manuel P. Soriaga, Kenneth L. Vieira and Arthur T. Hubbard, *J. Electroanal. Chem.*, **184**, 171 (1985).
85. Films Formed on Well-Defined Stainless Steel Single-Crystal Surfaces in Borate, Sulfate, Perchlorate and Chloride Solutions: Studies of the (111) Plane by LEED, Auger Spectroscopy and Electrochemistry. David A. Harrington, Andrzej Wieckowski, Stephen D. Rosasco, Ghaleb N. Salaita and Arthur T. Hubbard, *Langmuir*, **1**, 232 (1985).
86. Cation Competition in the Electrical Double-Layer at a Well-Defined Electrode Surface: Li^+ , Na^+ , K^+ , Cs^+ , H^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , La^{3+} , Tetramethyl Ammonium, Choline and Acetylcholine Cations at Pt(111) Surfaces Containing an Ordered Layer of Cyanide. Stephen D. Rosasco, John L. Stickney, Ghaleb N. Salaita, Douglas G. Frank, James Y. Katekaru, Bruce C. Schardt, Manuel P. Soriaga, Donald A. Stern and Arthur T. Hubbard, *J. Electroanal. Chem.*, **188**, 98 (1985).

87. Influence of Oriented Chemisorbed Monolayers on the Electrode Kinetics of Unadsorbed Redox Couples. James H. White, Manuel P. Soriaga and Arthur T. Hubbard, *J. Phys. Chem.*, **89**, 3227 (1985).
88. Reaction Mechanism of the Benzoquinone/Hydroquinone Couple at Pt Electrodes in Aqueous Solutions: Retardation and Enhancement of Electrode Kinetics by Single Chemisorbed Layers. James H. White, Manuel P. Soriaga, and Arthur T. Hubbard, *J. Electroanal. Chem.*, **185**, 331 (1985).
89. pH and Potential Dependence of the Electrical Double Layer at Well Defined Electrode Surfaces: Cs^+ and Ca^{2+} at $\text{Pt}(111)(2\sqrt{3}\times 2\sqrt{3})\text{R}30^\circ\text{-CN}^-$, $\text{Pt}(111)(\sqrt{13}\times\sqrt{13})\text{R}14^\circ\text{-CN}^-$ and $\text{Pt}(111)(2\times 2)\text{-SCN}^-$. Douglas G. Frank, James Y. Katekaru, Stephen D. Rosasco, Ghaleb N. Salaita, Bruce C. Schardt, Manuel P. Soriaga, Donald A. Stern, John L. Stickney and Arthur T. Hubbard, *Langmuir*, **1**, 587 (1985).
90. Characterization of Platinum Electrodes by Infrared Spectroscopy. Jay B. Benziger, F. A. Pascal, Steven L. Bernasek, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*, **198**, 65 (1985).
91. Effect of Non-aqueous Solvents on the Chemisorption and Orientation of Aromatic Compounds at Smooth Polycrystalline Platinum Electrodes: Naphtho-hydroquinone in Water-Benzene Solutions. Dian Song, Manuel P. Soriaga, Kenneth L. Vieira, Donald C. Zapien and Arthur T. Hubbard, *J. Phys. Chem.*, **89**, 3999 (1985).
92. Surface Coordination Chemistry of Well-Defined Platinum Electrodes: Surface** Polyprotic Acidity of $\text{Pt}(111)(2\sqrt{3}\times 2\sqrt{3})\text{R}30^\circ\text{-CNH}$. Bruce C. Schardt, John L. Stickney, Donald A. Stern, Douglas G. Frank, James Y. Katekaru, Stephen D. Rosasco, Ghaleb N. Salaita, Manuel P. Soriaga and Arthur T. Hubbard, *Inorg. Chem.*, **24**, 1419 (1985).
93. Effect of Non-Aqueous Solvents on the Chemisorption and Orientation of Aromatic Compounds at Smooth Polycrystalline Platinum Electrodes: Naphthohydroquinone and Tetrahydroxybiphenyl in Water-Acetonitrile Solutions. Dian Song, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*, **201**, 153 (1986).

94. Electrodeposition of Copper on Platinum (111) Surfaces Pretreated with Iodine.
** Studies by LEED, Auger Spectroscopy and Electrochemistry. John L. Stickney, Stephen D. Rosasco and Arthur T. Hubbard. In "The Chemistry and Physics of Electrocatalysis", J.D.E. McIntyre, M.J. Weaver and E.B. Yeager, Eds., The Electrochemical Society, Pennington, New Jersey, 1984 (Volume 84:12, pp 130-149).
95. Structure and Composition of a Platinum (111) Surface as a Function of pH and Electrode Potential in Aqueous Bromide Solutions. Ghaleb N. Salaita, Donald A. Stern, Frank Lu, Helmut Baltruschat, Bruce C. Schardt, John L. Stickney, Manuel P. Soriaga, Douglas G. Frank and Arthur T. Hubbard, *Langmuir*, 2, 828 (1986).
96. Ordered/Disordered Packing in Mixed Chemisorbed Layers: Vertically Oriented
** Polyphenolic Compounds at Smooth Polycrystalline Platinum Electrodes. Dian Song, Manuel P. Soriaga and Arthur T. Hubbard, *Langmuir*, 2, 20 (1986).
97. Order-Disorder Effects in Competitive Irreversible Adsorption of Aromatic
** Compounds at Platinum Electrodes: 1,4-Naphthohydroquinone and 2,2',5,5'-Tetrahydroxybiphenyl. Dian Song, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*, 193, 255 (1985).
98. Characterization of Single-Crystal Electrode Surfaces as a Function of Potential and pH by Auger Spectroscopy and LEED: Pt(111) in Aqueous CaCl_2 and HCl Solutions. Donald A. Stern, Helmut Baltruschat, Miriam Martinez, John L. Stickney, Dian Song, Scott K. Lewis, Douglas G. Frank and Arthur T. Hubbard, *J. Electroanal. Chem.*, 217, 101 (1987).
99. Kinetics of Oriented Adsorption: Hydroquinone on Platinum. Victor K.F. Chia,
** Manuel P. Soriaga and Arthur T. Hubbard, *J. Phys. Chem.*, 91, 78 (1987).
100. Electrochemical Surface Characterization. Arthur T. Hubbard, Victor K.F.
** Chia, Douglas G. Frank, James Y. Katekaru, Stephen D. Rosasco, Ghaleb N. Salaita, Bruce C. Schardt, Dian Song, Manuel P. Soriaga, Donald A. Stern, John L. Stickney, James H. White, Kenneth L. Vieira, Andrzej Wieckowski and Donald C. Zapien. In "New Dimensions in Chemical Analysis", B. L. Shapiro, Ed. (Texas A&M University Press, 1985), p. 135.
101. Electrodeposition of Pb onto Pt(111) Surfaces Containing Iodine Adlattices. Studies by Low-Energy Electron Diffraction and Auger Spectroscopy. John L. Stickney, Donald A. Stern, Bruce C. Schardt, Donald C. Zapien, Andrzej Wieckowski and Arthur T. Hubbard, *J. Electroanal. Chem.*, 213, 293 (1986).

102. Electrodposition of Sn onto a Well-Defined Pt(111) Surface from Aqueous HBr
** Solutions: Studies by LEED and Auger Spectroscopy. John L. Stickney, Bruce C. Schardt, Donald A. Stern, Andrzej Wieckowski and Arthur T. Hubbard, *J. Electrochem. Soc.*, 133, 648 (1986).
103. Electrodposition of Pb onto Pt(111) in Aqueous Bromide Solutions. Studies by LEED and Auger Spectroscopy. Bruce C. Schardt, John L. Stickney, Donald A. Stern, Andrzej Wieckowski, Donald C. Zapien and Arthur T. Hubbard, *Langmuir*, 3, 239 (1987).
104. Electrodposition of Pb onto Pt(111) in Aqueous Chloride Solutions. Studies
** by LEED and Auger Spectroscopy. Bruce C. Schardt, John L. Stickney, Donald A. Stern, Andrzej Wieckowski, Donald C. Zapien and Arthur T. Hubbard, *Surf. Sci.*, 175, 520 (1986).
105. The Influence of Organic Solvents on Aromatic Adsorption at Platinum: Acetic
** Acid, Acetone, Acetonitrile, Dimethylacetamide, Dimethylsulfoxide, Sulfolane and Tetrahydrofuran. Dian Song, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electrochem. Soc.*, 134, 874 (1987).
106. Analysis of Products from Reactions of Chemisorbed Monolayers at Smooth Platinum Electrodes: Electrochemical Hydrodesulfurization of Thiophenol Derivatives. Kenneth L. Vieira, Donald C. Zapien, Manuel P. Soriaga, Arthur T. Hubbard, Karen P. Low and Stanley E. Anderson, *Anal. Chem.*, 58, 2964 (1986).
107. Structure of the Solid-Liquid Interface. Arthur T. Hubbard, in "Comprehensive
** Chemical Kinetics", C. H. Bamford, D. F. H. Tipper and R. G. Compton, Ed., Volume 28, Chapter 1, Elsevier, Amsterdam (1988).
108. The Kinetics of Hydroquinone Chemisorption at Polycrystalline Platinum Electrodes. The Effect of Surface Roughness. Victor K. F. Chia, James H. White, Manuel P. Soriaga and Arthur T. Hubbard, *J. Electroanal. Chem.*, 217, 121 (1987).
109. Films Formed on Stainless Steel Single-Crystal Surfaces in Aqueous Solutions: Studies of the (100) Plane by LEED, Auger Spectroscopy and Electrochemistry. Douglas G. Frank, Victor K. F. Chia, Mark Schneider and Arthur T. Hubbard, *Langmuir*, 3, 860 (1987).

110. Structure and Composition of the Pt(s)[6(111)x(111)] Step-Terrace Surface vs. pH and Potential in Aqueous Br⁻ Solutions. Studies by LEED and Auger Spectroscopy. Helmut Baltruschat, Miriam Martinez, Scott K. Lewis, Frank Lu, Dian Song, Donald A. Stern, Arunabha Datta and Arthur T. Hubbard, *J. Electroanal. Chem.*, **217**, 111 (1987).
111. Adlattice Structure and Hydrophobicity of Pt(111) in Aqueous Potassium Iodide Solutions: Influence of pH and Electrode Potential. Frank Lu, Ghaleb N. Salaita, Helmut Baltruschat and Arthur T. Hubbard, *J. Electroanal. Chem.*, **222**, 305 (1987).
112. Adsorption of Ferricyanide at Pt(111) as a Function of Electrode Potential Studied by Auger Spectroscopy. Helmut Baltruschat, Frank Lu, Dian Song, Scott K. Lewis, Donald C. Zapien, Douglas G. Frank, Ghaleb N. Salaita and Arthur T. Hubbard, *J. Electroanal. Chem.*, **234**, 229 (1987).
113. First Birthday. Arthur T. Hubbard, *Langmuir*, **2**, 1 (1986).
114. Structure and Composition of the Ag(111) Surface as a Function of Electrode
** Potential in Aqueous Halide Solutions. Ghaleb N. Salaita, Frank Lu, Laarni Laguren-Davidson and Arthur T. Hubbard, *J. Electroanal. Chem.*, **229**, 1 (1987).
115. Electrodeposition of Tl, Pb, Bi, and Cu on Ag(111) from Aqueous Solutions.
** Studies by Auger Spectroscopy and LEED. Laarni Laguren-Davidson, Frank Lu, Ghaleb N. Salaita and Arthur T. Hubbard, *Langmuir*, **4**, 224 (1988).
116. "Paul Billoen, 1939-1986", Arthur T. Hubbard, *Langmuir*, **3**, 306 (1987).
117. Characterization of Hydroquinone and Related Compounds Adsorbed at Pt(111)
** from Aqueous Solutions: Electron Energy-Loss Spectroscopy, Auger Spectroscopy, Low-Energy Electron Diffraction and, Cyclic Voltammetry. Frank Lu, Ghaleb N. Salaita, Laarni Laguren-Davidson, Donald A. Stern, Edna Wellner, Douglas G. Frank, Nikola Batina, Donald C. Zapien, Nicholas Walton and Arthur T. Hubbard, *Langmuir*, **4**, 637 (1988).
118. Adsorbed Thiophenol and Related Compounds Studied at Pt(111) Electrodes by EELS, Auger Spectroscopy and Cyclic Voltammetry. Donald A. Stern, Edna Wellner, Ghaleb N. Salaita, Laarni Laguren-Davidson, Frank Lu, Nikola Batina, Douglas G. Frank, Donald C. Zapien, Nicholas Walton and Arthur T. Hubbard, *J. Amer. Chem. Soc.*, **110**, 4885 (1988).

119. Electrochemical Reactivity of 2,2',5,5'-Tetrahydroxybiphenyl and Related Compounds Adsorbed at Pt(111) Surfaces: Studies by EELS, LEED, Auger Spectroscopy and Cyclic Voltammetry. Ghaleb N. Salaita, Laarni Laguren-Davidson, Frank Lu, Nicholas Walton, Edna Wellner, Donald A. Stern, Nikola Batina, Douglas G. Frank, Chiu-Hsun Lin, Clifford S. Benton and Arthur T. Hubbard, *J. Electroanal. Chem.*, **245**, 253 (1988).
120. Oriented Adsorption at Well-Defined Electrode Surfaces Studied by Auger LEED and EELS Spectroscopy. Nikola Batina, Douglas G. Frank, John Y. Gui, Bruce E. Kahn, Chiu-Hsun Lin, Frank Lu, James W. McCargar, Ghaleb N. Salaita, Donald A. Stern, Donald C. Zapien and Arthur T. Hubbard, Proceedings of the 4th International Fischer Symposium, *Electrochim. Acta.*, **34**, 1031 (1989).
121. Studies of L-Dopa and Related Compounds Adsorbed from Aqueous Solutions at Pt(100) and Pt(111): Electron Energy-Loss Spectroscopy, Auger Spectroscopy, and Electrochemistry. Donald A. Stern, Ghaleb N. Salaita, Frank Lu, James W. McCargar, Nikola Batina, Douglas G. Frank, Laarni Laguren-Davidson, Chiu-Hsun Lin, Nicholas Walton, John Y. Gui and Arthur T. Hubbard, *Langmuir*, **4**, 711 (1988).
122. Reversible Redox of 2,5-Dihydroxythiophenol Chemisorbed on Gold and Platinum Electrodes: Evidence for Substrate-Mediated Adsorbate-Adsorbate Interactions. Beatriz G. Bravo, Thomas Mebrahtu, Manuel P. Soriaga, Donald C. Zapien, Arthur T. Hubbard and John L. Stickney, *Langmuir*, **3**, 595 (1987).
123. Studies of Adsorbed Organic Molecules at Well-Defined Pt(111) Electrode Surfaces by LEED, Auger, EELS and Electrochemistry. Ghaleb N. Salaita, Frank Lu, Laarni Laguren-Davidson, Douglas G. Frank, Donald A. Stern, Donald C. Zapien, Nikola Batina, Edna Wellner, Nicholas Walton and Arthur T. Hubbard, in "Chemically Modified Surfaces", Volume 2, D. Leyden, Ed., Gordon and Breach, New York (1987).
124. Electrochemistry at Well-Characterized Surfaces. Arthur T. Hubbard, *Chem. Revs.*, **88**, 633 (1988).
125. Potential-Dependent Surface Chemistry of 3-Pyridine Carboxylic Acid (Niacin) and Related Compounds at Pt(111) Electrodes. Donald A. Stern, Laarni Laguren-Davidson, Douglas G. Frank, John Y. Gui, Chiu-Hsun Lin, Frank Lu, Ghaleb N. Salaita, Nicholas Walton, Donald C. Zapien and Arthur T. Hubbard, *J. Amer. Chem. Soc.*, **111**, 877 (1989).

126. Comparison of Vacuum-Annealed and Electrochemically Cycled Electrodes in
** Adsorption and Electrocatalysis: Aromatic Compounds at Platinum (111)
and Polycrystalline Platinum. John Y. Gui, Bruce E. Kahn, Laarni
Laguren-Davidson, Chiu-Hsun Lin, Frank Lu, Ghaleb N. Salaita, Donald A.
Stern and Arthur T. Hubbard, *Langmuir*, 5, 819 (1989).
127. Structure and Composition of Pt(111) and Pt(100) Surface as a Function of
** Electrode Potential in Aqueous Sulfide Solutions. Nikola Batina, James W.
McCargar, Laarni Laguren-Davidson, Chiu-Hsun Lin and Arthur T. Hubbard,
Langmuir, 5, 123 (1989)
128. Surface Electrochemistry of Amino Acids: Voltammetry Assisted by EELS,
** Auger Spectroscopy and LEED. Arthur T. Hubbard, Douglas G. Frank, Donald
A. Stern, Michael J. Tarlov, Nikola Batina, Nicholas Walton, Edna Wellner and
James W. McCargar. In "Redox Chemistry and Interfacial Behavior of
Biological Molecules", G. Dryhurst and K. Niki, Ed., Plenum, New York,
(1988), page 229.
129. Studies of Thiophene and Substituted Thiophenes at Pt(111) Electrodes by
** Vibrational Spectroscopy (EELS) and Auger Spectroscopy: Monomers, Dimers
and Polymers. Nikola Batina, John Y. Gui, Bruce E. Kahn, Chiu-Hsun Lin,
Frank Lu, James W. McCargar, Ghaleb N. Salaita, Donald A. Stern, Arthur T.
Hubbard, Harry B. Mark, Jr., and Hans Zimmer, *Langmuir* 5, 588 (1989).
130. Molecular Adsorption at Well-Defined Pt Surfaces: Voltammetry Assisted by
** Auger Spectroscopy, EELS and LEED. Arthur T. Hubbard, Donald A. Stern,
Ghaleb N. Salaita, Douglas G. Frank, Frank Lu, Laarni Laguren-Davidson,
Nikola Batina, Donald C. Zapien, in "Molecular Phenomena at Electrode
Surfaces", Manuel P. Soriaga, Ed., A. C. S. Symposium Series, #378,
Chapter 2, p. 29 (1988).
131. Studies of Electroactive Adsorbates by Cyclic Voltammetry Assisted by
** Vibrational Spectroscopy (EELS) and Auger Spectroscopy: (2-Pyridyl)
Hydroquinone, (3-Pyridyl) Hydroquinone and (4-Pyridyl) Hydroquinone a
Pt(111). Donald C. Zapien, John Y. Gui, Bruce E. Kahn, Chiu-Hsun Lin,
Frank Lu, Ghaleb N. Salaita, Donald A. Stern and Arthur T. Hubbard,
Inorg. Chem.

132. Studies of Adsorbed Unsaturated Alcohols at Well-Defined Pt(111) Electrode Surfaces by Cyclic Voltammetry Assisted by Vibrational Spectroscopy (EELS) and Auger Spectroscopy. John Y. Gui, Bruce E. Kahn, Chiu-Hsun Lin, Frank Lu, Ghaleb N. Salaita, Donald A. Stern, Donald C. Zapien and Arthur T. Hubbard, *J. Electroanal. Chem.*, 252, 169 (1988).
133. Adsorption of Bipyridyls, Biphenyls, Phenylpyridines, and Carboxylic Acid Derivatives at Pt(111) Electrodes: Studies by Vibrational Spectroscopy (EELS), Auger Spectroscopy, and Electrochemistry. Scott A. Chaffins, John Y. Gui, Bruce E. Kahn, Chiu-Hsun Lin, Frank Lu, Ghaleb N. Salaita, Donald A. Stern, Donald C. Zapien and Arthur T. Hubbard, *Langmuir*.
134. Adsorbed Organic Molecules at Well-Defined Electrode Surfaces. Ghaleb N. Salaita and Arthur T. Hubbard, in "Molecular Design of Electrode Surfaces", Royce Murray, Editor, John Wiley, New York (1989).
135. Imaging Surface Atomic Structure by Means of Auger Electrons. Douglas G. Frank, Nikola Batina, John Rovang, and Arthur T. Hubbard, *Science*.
136. Letter from America. Arthur T. Hubbard, *Eur. Spectrosc. News*, 78, 28 (1988).
137. Comparison of the Voltammetric Behavior of Adsorbed or Dissolved Unsaturated Alcohols at Vacuum-Annealed and Electrochemically Cycled Pt(111) and Pt(polycrystalline) Electrodes. Nikola Batina, Bruce E. Kahn, Chiu-Hsun Lin, James W. McCargar, Ghaleb H. Salaita, and Arthur T. Hubbard, *Electroanalysis*, 1, 213 (1989).
138. Electrochemical Oxidation of Adsorbed Alkenoic Acids as a Function of Chain Length at Pt(111) Electrodes: Studies by Cyclic Voltammetry, EELS and Auger Spectroscopy. Nikola Batina, Scott A. Chaffins, Bruce E. Kahn, Frank Lu, James W. McCargar, John Rovang, Donald A. Stern and Arthur T. Hubbard, *Catalysis Letters*.
139. Multi-nitrogen Heteraromatics Studied at Pt(111) Surfaces by EELS, Auger Spectroscopy and Electrochemistry: Pyrazine, Pyrimidine, Pyridazine, 1,3,5-Triazine and Carboxylic Acid Derivations. Scott A. Chaffins, John Y. Gui, Chiu-Hsun Lin, Frank Lu, Ghaleb N. Salaita, Donald A. Stern, and Arthur T. Hubbard, *Langmuir*.

140. Direct Imaging of Surface Atomic Structure by Angular Distribution Auger
** Microscopy (ADAM): The Bare Pt(111) Surface. Douglas G. Frank, Nikola Batina, James W. McCargar and Arthur T. Hubbard, *Langmuir*, 5, 1141 (1989).
141. Electrochemical Oxidation of Adsorbed Terminal Alkenols as a Function of
** Chain Length at Pt(111) Electrodes. Studies by Cyclic Voltammetry, EELS and Auger Spectroscopy. Nikola Batina, Scott A. Chaffins, Frank Lu, James W. McCargar, John W. Rovang, Donald A. Stern and Arthur T. Hubbard, *J. Electroanal. Chem.*
142. Electrochemical Oxidation of Adsorbed Terminal Alkenes as a Function of
** Chain Length at Pt(111) Electrodes. Studies by Cyclic Voltammetry, EELS and Auger Spectroscopy. Nikola Batina, Scott A. Chaffins, Frank Lu, James W. McCargar, John Rovang, Donald A. Stern and Arthur T. Hubbard, *J. Electroanal. Chem.*
143. Surface Chemistry of Five-Membered Heteroaromatics at Pt(111) Electrodes
** Studied by EELS, LEED, Auger Spectroscopy and Electrochemistry: Furan, Pyrrole, and Thiophene. John Y. Gui, Donald A. Stern, Frank Lu and Arthur T. Hubbard, *J. Electroanal. Chem.*
144. Studies of Hydroxypyridines and Pyridyl Alcohols at Pt(111) Electrode Surfaces
** by EELS, Auger Spectroscopy and Electrochemistry, Scott A. Chaffins, John Y. Gui, Ping Gao, Chiu Hsun Lin, Frank Lu, Ghaleb N. Salaita, Donald A. Stern and Arthur T. Hubbard, *Langmuir*.
145. ** Atomic Imaging with Auger Electrons. Arthur T. Hubbard, *Accts. Chem. Res.*
146. Surface Vibrational Spectroscopy. A Comparison of the EELS Spectra of
** Organic Adsorbates at Pt(111) with IR and Raman Spectra of the Unadsorbed Organics. B. E. Kahn, S. A. Chaffins, J. Y. Gui, F. Lu, D. A. Stern, and A. T. Hubbard, *Chemical Physics*, 141, 21 (1990).
147. Surface Chemistry of Mercaptopyridines at Ag(111) Electrodes Studied by EELS,
** LEED, Auger Spectroscopy and Electrochemistry J. Y. Gui, F. Lu, D.A. Stern, and A. T. Hubbard, *J. Electroanal. Chem.*
148. Surface Electrochemistry (Kendall Award Address, American Chemical Society,
** 1989), Arthur T. Hubbard, *Langmuir*, 6, 97 (1990).
149. Molecular Electrochemistry at Well-Defined Surfaces: Studies of Organics at
** Pt(111) by Auger, EELS, LEED and Electrochemistry. Ghaleb N. Salaita, Chiu-Hsun Lin, Ping Gao, and Arthur T. Hubbard, *Arabian Journal for Science and Engineering*, 15, 319 (1990).
150. Direct Imaging of Surface Atomic Structure by Angular Distribution Auger

- **** Microscopy (ADAM): Monolayers and Films of Ag at Pt(111) Pretreated with Iodine. Douglas G. Frank, Nikola Batina, Teresa Golden, Frank Lu and Arthur T. Hubbard, *J. Phys. Chem.*
151. Adsorption and Surface Structural Chemistry of Thiophenol Benzyl Mercaptan and Alkyl Mercaptans. Comparative Studies at Ag(111) and Pt(111) Electrodes by Means of Auger, EELS, LEED and Electrochemistry. John Y. Gui, Donald A. Stern, Douglas G. Frank, Frank Lu, Donald C. Zapien and Arthur T. Hubbard, *Langmuir*.
- **** 152. Direct Imaging of Pt(111) Surface Atomic Structure by Angular Distribution Auger Microscopy (ADAM): Influence of Auger Electron Kinetic Energy. Douglas G. Frank, Nikola Batina, Teresa Golden, Oliver Chyan and Arthur T. Hubbard, *Langmuir*.
153. Direct Imaging of Pt(111) Surface Atomic Structure by Angular Distribution Auger Microscopy (ADAM): Influence of Temperature. Douglas G. Frank, Nikola Batina, Teresa Golden, Oliver Chyan and Arthur T. Hubbard, *J. Phys. Chem.*
154. Direct Imaging of Epitaxial Layers by Angular Distribution Auger Microscopy. ****** Douglas G. Frank, Frank Lu, Teresa Golden and Arthur T. Hubbard, *Mater. Res. Soc. Bull.*, page 19, May, 1990.
155. Direct Imaging of Adsorbed Methyl Mercaptan by Angular Distribution Auger Microscopy (ADAM). Douglas G. Frank, Oliver Chyan, Teresa Golden and Arthur T. Hubbard, *Langmuir*.
156. Direct Imaging of Ag(111) Surface Atomic Structure by Angular Distribution Auger Microscopy (ADAM) Influence of Auger Electron Kinetic Energy. Oliver Chyan, Douglas G. Frank, Teresa Golden and Arthur T. Hubbard.
157. Direct Imaging of Surface Atomic Structure by Angular Distribution Auger ****** Microscopy (ADAM): Electrodeposited Ag at Bare Pt(111). Oliver Chyan, Douglas G. Frank, Teresa Golden and Arthur T. Hubbard, *J. Electroanal. Chem.*
158. Studies of Adsorbed Saturated Alcohols at Pt(111) Electrodes by Vibrational ****** Spectroscopy (EELS), Auger Spectroscopy and Electrochemistry. Ping Gao, Chiu-Hsun Lin, Ghaleb N. Salaita, James H. White, Scott A. Chaffins and Arthur T. Hubbard, *Langmuir*.
159. Imaging Surface Atomic Structure by Means of Auger Electrons. Arthur T. ****** Hubbard, Douglas G. Frank, Oliver M. R. Chyan and Teresa Golden, *J. Vac. Sci. Tech. (34th International Symposium on Electron, Ion and Photon Beams)*.
160. Response (Technical Comments). Douglas G. Frank, Teresa Golden and Arthur T.

- ** Hubbard, *Science*, 248, 1129 (1990).
161. Imaging Surface Atomic Layers by Means of Auger Electrons. Nikola Batina,
- ** Oliver M. R. Chyan, Douglas G. Frank, Teresa Golden and Arthur T. Hubbard,
Naturwissenschaften.

III. REFERENCES TO OTHER WORK

162. J. E. Demuth, K. Christman and P.N. Sanda, *Chem. Phys. Letters*, **76**, 201 (1980).
163. V. H. Grassian and E. L. Muetterties, *J. Phys. Chem.*, **90**, 5900 (1986).
164. M. Surman, S.R. Bare, P. Hoffman and D.A. King, *Surface Sci.*, **179**, 243 (1987).
165. R. J. Waltman, J. Bargon and A. F. Diaz, *J. Phys. Chem.*, **87**, 1459 (1983).
166. A. R. Hillman and E. F. Mallen, *J. Electroanal. Chem.*, **243**, 403 (1988).
167. P. A. Christensen and A. Hammett, *J. Electroanal. Chem.*, **242**, 47 (1988).
168. H. Neugebauer, G. Nauer, A. Neckel, G. Tourillon, F. Garnier and P. Lane, *J. Phys. Chem.*, **88**, 652 (1984).
169. T. A. Skotheim, ed. "Handbook of Conducting Polymers", Volume I, Chs. 3 and 9 (Marcel Dekker, N.Y., 1986).
170. G. Tourillon, E. Dargyge, A. Fontaine, P. Garrett, M. Sagurton, P. Xu and G.P. Williams, *Europhysics Letters*, **4**, 1391 (1987).
171. F. Zaera, E.B. Kollin and J.L. Gland, *Langmuir*, **3**, 555 (1987).
172. J. F. Lang and R. I. Masel, *Surface Sci.*, **183**, 44 (1987).
173. E. S. Kirkor, D. E. David, T. F. Magnera and J. Michl, *Langmuir*, **4**, 578 (1988).
174. R. R. Adzic, A. V. Tripkovic and V. B. Vesovic, *J. Electroanal. Chem.*, **204**, 329 (1986).
175. S. Motoo and N. Furuya, *J. Electroanal. Chem.*, **197**, 209 (1986).
176. (a) J. Clavilier and S. G. Sun, *J. Electroanal. Chem.*, **199**, 471 (1986);
(b) S. G. Sun and J. Clavilier, *ibid*, **236**, 95 (1987);
(c) S. G. Sun, J. Clavilier and A. Bewick, *ibid*, **240**, 147 (1988).
177. L. Stolberg, J. Lipkowski and D.E. Irish, *J. Electroanal. Chem.*, **238**, 333 (1987).
178. L. M. Rice, E. K. Kranskopf and A. Wieckowski, *J. Electroanal. Chem.*, **239**, 413 (1988).
179. (a) Z. Borowska and A. Hamelin, *J. Electroanal. Chem.*, **241**, 373 (1988);
(b) E. Dutkiewicz, P. Skoluda and A. Hamelin, *J. Electroanal. Chem.*, **240**, 291 (1988).
180. G. Kokkinidis, J. M. Legar, and C. Lamy, *J. Electroanal. Chem.*, **242**, 221 (1988).

IV. SCIENTIFIC PERSONNEL

Arthur Case. Machinist. Ohio College of Applied Science, 1978–1982. US Precision Lens, 1982–1986.

Oliver Chyan. Postdoctoral Research Chemist. BS, 1980, National Chung Hsing University; MS, 1982, National Taiwan University; MS, 1984, University of Texas, Arlington; Ph.D., 1989, Massachusetts Institute of Technology.

Frank B. Douglas. Electronics Engineer. BS, 1980, University of Cincinnati. US Precision Lens, 1980–1985; Spectraphysics, 1985–1988.

Douglas G. Frank. Graduate Student. BS, 1984, Westmont College; Ph.D., 1990, University of Cincinnati.

Ping Gao. Postdoctoral Research Chemist. BS, 1982, Nanjing Normal University; Ph.D., 1989, Purdue University.

Teresa Golden. Postdoctoral Research Chemist. BS, 1985, Texas Technological University; Ph.D., 1990, New Mexico State University.

John Y. Gui. Postdoctoral Research Chemist. BS, 1982, Wuhan University; Ph.D., 1987, Ohio State University.

Douglas Hurd. Machinist. Kentucky State Vocational School, 1961–62. Procter and Gamble Company, 1968–1988.

Chiu-Hsun Lin. Postdoctoral Research Chemist. BS, 1979, National Taiwan Normal University; Ph.D., 1987, Texas A&M University.

Richard Shaw. Technical Assistant. BS, 1977; MS, 1985, Bowling Green State University.

Donald A. Stern. Graduate Student. BS, 1980, University of California Santa Barbara.

Vickie Townsend. Assistant to the Ohio Eminent Scholar. Procter & Gamble Company, 1967–1972; University of Cincinnati, 1972–present.

James White. Postdoctoral Research Chemist. BS, 1982, California Polytechnic State University; Ph.D., 1986, University of California Santa Barbara.

Donald C. Zapien. Graduate Student. BS, 1980, University of Santa Clara.

V. CURRENT SUPPORT —ARTHUR T. HUBBARD

Gas Research Institute.

"Electrocatalyst Surfaces".

December, 1986 — November, 1989 \$359,500

January, 1990 — December, 1991 \$423,807

Air Force Office of Scientific Research, SR86-0200.

"Electrochemistry of Molecules Attached to Metal Surfaces".

May, 1987 — April, 1988 \$148,994

May, 1988 — April, 1989 \$156,443

May, 1989 — April, 1990 \$171,414

May, 1990 — April, 1991 \$120,649

Department of Energy.

"Surface Chemistry of Electrocatalysts".

July, 1986 — July, 1988 \$167,670

August, 1988 — July, 1989 \$112,955

August, 1989 — July, 1990 \$ 60,000

National Institutes of Health. 5 R01 GM38311

"Interfacial Electrochemistry of Biomolecules".

January — December, 1987. \$101,727

January — December, 1988. \$104,546

January — December, 1989 \$108,573

January — December, 1990 \$112,203

National Science Foundation

"Electrochemistry at Well-Defined Surfaces"

June, 1987 — May, 1988 \$145,000

June, 1988 — May, 1989 \$145,000

June, 1989 — May, 1990 \$225,000

June, 1990 — May, 1991 \$151,900

United Technologies Pratt & Whitney (Lehr Precision)

"Titanium Alloy Study"

December, 1988 — March, 1989 \$ 30,000

January, 1990 — December, 1991 \$320,000